Development of a Waste-Free Technology for Processing Biowastes into High Valuable Chemicals and Carbon materials

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DISSERTATION

For the degree of Doctor of Natural Sciences

- Dr rer. nat. -

of the Faculty of Mathematics and Natural Sciences,

Carl von Ossietzky University of Oldenburg.

Accepted Dissertation

by

Olayinka Ahmed Ibitowa

Born on 19.01.1991 in Lagos Nigeria

This work was conducted by me from January 2020 to December 2023 at the School of Technical Chemistry, within the Faculty of Mathematics and Natural Sciences at Carl von Ossietzky University of Oldenburg, under the guidance of Prof. Dr. Michael Wark.

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ABSTRACT

Poultry litters, comprising chicken manure and sawdust, are significant byproducts of the poultry industry. Escalating poultry production has led to increased accumulation of these litters, presenting both opportunities and challenges for waste management. Chicken manure is nutrient-rich, enhancing soil fertility, while sawdust provides carbon, aiding in composting and soil structure improvement. However, improper management of poultry litters can lead to environmental issues such as nutrient leaching, water contamination, and greenhouse gas emissions. Therefore, innovative solutions are required to transform this waste into valuable resources, promoting sustainable practices and environmental stewardship.

This study investigates several waste-free technologies, including hydrothermal carbonization (HTC), its modified two-step process (Two-step HTC), vapourthermal carbonization (VTC), and direct steam activation (ST), to convert poultry litters into valuable products such as hydrochar and hydroxymethylfurfural (5-HMF). The research aims to optimize 5-HMF production and enhance the specific surface area (SSA) of the hydrochar through further steam activation, turning the hydrochar into activated hydrochar, addressing environmental concerns and contributing to a circular bioeconomy. Poultry litters with varying proportions of chicken manure and sawdust (S, S67M33, S50M50, S33M67, M) were utilized to compare standard HTC, modified two-step HTC, VTC, and ST under different temperatures and retention times.

HTC converts organic waste into char, liquids, and gases under high temperature and pressure in the presence of water, mimicking natural coal formation. The modified two-step HTC process includes an initial hydrothermal pretreatment at milder temperatures, followed by replacing the resulting liquor with fresh water before the final HTC step, aiming to mitigate HTC disadvantages, such as producing heavily polluted process water, long reaction times, and high operating pressures. VTC, using superheated steam, significantly reduces process water volume, while ST involves direct carbonization without prior treatment, offering a time-efficient alternative.

Key findings indicate that the two-step HTC method significantly enhances 5-HMF production compared to other technologies. Sawdust particularly aids 5-HMF production, while chicken

manure impedes it. Optimal conditions were identified: hydrothermal pretreatment at 150 °C for 3 hours and hydrothermal carbonization at 220 °C for 1 hour, producing up to 15.3 g/l of 5-HMF from sawdust compared to the initial 9.2 g/l produced using HTC. Conversely, insignificant amounts of 5-HMF were produced from chicken manure under HTC conditions. The two-step HTC method also effectively reduced total organic carbon (TOC) present in the process water, a significant advantage over standard HTC. Furthermore, the process water produced by HTC was found to foster algae growth, aiding in reducing TOC levels and achieving a more sustainable waste treatment approach. Methods involving no water interaction yielded no 5-HMF but allowed for the analysis of activated char.

Results showed that standard HTC at 220 °C for 2 hours followed by activation at 650 °C is sufficient to produce activated hydrochars with high SSA. The SSA increases with the proportion of sawdust, while chicken manure contributes to mesoporous development. VTC-treated chars exhibited more pronounced mesopores compared to HTC regardless of feedstock proportion, attributed to vapour's influence on pore arrangement. While HTC produced significant organic process water, further reduction was achieved using the two-step HTC, and VTC effectively minimized it.

Activated carbon production was explored through HTC and ST. HTC conditions of 200 and 220 °C for 2 and 4 hours, followed by activation at 650 °C, resulted in highly porous carbon. Similar activated carbon was produced via ST without pretreatment at 750 °C, resulting in a higher porosity up to macropores and SSA. Comparative analysis highlighted that HTC produced activated chars with microporosity, while ST yielded chars with higher pore development (meso – macro pores) and SSA. Notably, HTC produced higher SSA from chicken manure (488 m^2/g) compared to ST (216 m^2/g), but ST surpassed HTC in SSA from sawdust (824 m^2/g vs. 660 m^2/g). One major drawback of ST is the relatively low yield of 18 % compared to the 53 % obtained in HTC. With the use of ST, it was possible to create a large amount of meso- and macro- pores with pore volumes (PV) of 0.80 and 6.40 cm^3/g respectively, while carbon material produced via HTC contains mainly micropores.

Pyrolytic Carbonization (PYC) demonstrated the ability to generate activated char similar to ST, with marginal increases in SSA and pore volume. PYC achieved a high yield of 83 %, addressing ST's low yield limitation. Activated char from PYC exhibited similar pore structures and SSA, indicating PYC's efficacy in achieving comparable properties with higher yields.

Applications of activated char in sodium-ion batteries were explored. Capacitance results showed that carbon electrodes from ST and PYC, with higher SSA and mesopores, exhibited larger capacitance up to 128 mAh/g compared to the relatively low capacitance obtained from HTC carbon-electrode ranging from 1 to 4 mAh/g. The capacitance produced from ST carbon-electrode materials was also compared to an industrial carbon black, showing better capacitance than electrode material produced from the industrial carbon black.

Activated char's potential for water purification was examined through methylene blue dye absorption experiments. Results revealed complete dye absorption by ST and PYC activated chars within 60 minutes, indicating superior water purification efficiency compared to HTC-derived chars, which displayed insignificant absorption after 300 minutes. This suggests that activated chars with high meso-macro pores, as seen in ST, PYC, and VTC, hold promising potential for water treatment applications.

This study successfully pioneers advancements in biowaste conversion through various carbonization methodologies, including HTC, Two-step HTC, VTC, ST, and PYC. The focus on diverse feedstocks, particularly poultry litters (PL) comprising sawdust and chicken manure, unveils promising avenues for value-added chemical production and carbon material synthesis. This findings emphasizes the significance of methodological intricacies and feedstock nuances, with VTC, ST, and PYC emerging as promising contenders for carbon materials and the two-step HTC standing out as an effective tool for optimizing chemical yields while mitigating environmental concerns. HTC's production of process water also supports algae growth, contributing to a more sustainable waste treatment approach. This research contributes to the scientific understanding of carbonization processes and advocates for eco-friendly technologies, focusing on minimizing environmental impact and maximizing resource efficiency.

ZUSAMMENFASSUNG

Geflügelstreu, bestehend aus Hühnermist und Sägemehl, stellt bedeutende Nebenprodukte der Geflügelindustrie dar. Die zunehmende Geflügelproduktion hat zu einer verstärkten Akkumulation dieser Streumaterialien geführt, die sowohl Chancen als auch Herausforderungen für das Abfallmanagement darstellen. Hühnermist ist nährstoffreich und verbessert die Bodenfruchtbarkeit, während Sägemehl Kohlenstoff liefert und die Kompostierung sowie die Bodenstrukturverbesserung unterstützt. Eine unsachgemäße Verwaltung von Geflügelstreu kann jedoch zu Umweltproblemen wie Nährstoffauslaugung, Wasserkontamination und Treibhausgasemissionen führen. Daher sind innovative Lösungen erforderlich, um diese Abfälle in wertvolle Ressourcen umzuwandeln, die nachhaltige landwirtschaftliche Praktiken und Umweltschutz fördern.

Diese Studie untersucht mehrere abfallfreie Technologien, darunter die hydrothermale Karbonisierung (HTC), ihr modifizierter zweistufiger Prozess (Zwei-Stufen HTC), die Dampfthermale Karbonisierung (VTC) und die direkte Dampfaktivierung (ST), um Geflügelstreu in wertvolle Produkte wie Hydrochar und Hydroxymethylfurfural (5-HMF) umzuwandeln. Die Forschung zielt darauf ab, die 5-HMF-Produktion zu optimieren und die spezifische Oberfläche (SSA) des Hydrochars durch weitere Dampfaktivierung zu erhöhen, wodurch der Hydrochar in aktivierten Hydrochar umgewandelt wird. Dies trägt zur Lösung umweltbezogener Probleme bei und fördert die Kreislaufwirtschaft. Geflügelstreu mit variierenden Anteilen von Hühnermist und Sägemehl (S, S67M33, S50M50, S33M67, M) wurde verwendet, um Standard HTC, modifizierten Zwei-Stufen HTC, VTC und ST unter verschiedenen Temperaturen und Verweilzeiten zu vergleichen.

HTC wandelt organische Abfälle unter hohen Temperaturen und Drücken in Gase, Flüssigkeiten und Kohle um, in Gegenwart von Wasser, was natürliche Kohlebildung nachahmt. Der modifizierte Zwei-Stufen HTC-Prozess umfasst eine anfängliche hydrothermale Vorbehandlung bei milderen Temperaturen, gefolgt von der Ersetzung des resultierenden Wassers durch Frischwasser vor dem finalen HTC-Schritt, um HTC-Nachteile wie die Erzeugung stark verschmutzten Prozesswassers, lange Reaktionszeiten und hohe Betriebsdrücke zu mildern. VTC

nutzt überhitzten Dampf, um das Prozesswasservolumen signifikant zu reduzieren, während ST eine direkte Karbonisierung ohne vorherige Behandlung darstellt und eine zeiteffiziente Alternative bietet.

Die wichtigsten Ergebnisse zeigen, dass der Zwei-Stufen HTC-Prozess die 5-HMF-Produktion signifikant im Vergleich zu anderen Technologien steigert. Insbesondere Sägemehl fördert die 5-HMF-Produktion, während Hühnermist diese hemmt. Optimale Bedingungen wurden identifiziert: hydrothermale Vorbehandlung bei 150 °C für 3 Stunden und hydrothermale Karbonisierung bei 220 °C für 1 Stunde, wodurch bis zu 15,3 g/l 5-HMF aus Sägemehl produziert wurden im Vergleich zu den initialen 9,2 g/l, die mit HTC produziert wurden. Im Gegensatz dazu wurden unter HTC-Bedingungen vernachlässigbare Mengen an 5-HMF aus Hühnermist produziert. Der Zwei-Stufen HTC-Prozess reduzierte auch effektiv den Gesamtkohlenstoffgehalt (TOC) im Prozesswasser, ein wesentlicher Vorteil gegenüber dem Standard HTC. Darüber hinaus wurde festgestellt, dass das bei HTC produzierte Prozesswasser das Wachstum von Algen fördert, was zur Reduzierung der TOC-Werte beiträgt und einen nachhaltigeren Behandlungsansatz für Abfälle ermöglicht. Methoden ohne Wasserinteraktion führten nicht zur Produktion von 5-HMF, erlaubten jedoch die Analyse von aktivierter Kohle.

Die Ergebnisse zeigten, dass Standard HTC bei 220 °C für 2 Stunden, gefolgt von einer Aktivierung bei 650 °C, ausreichte, um aktivierten Hydrochar mit hoher SSA zu produzieren. Die SSA erhöhte sich mit dem Anteil von Sägemehl, während Hühnermist zur Entwicklung mesoporöser Strukturen beitrug. VTC-behandelte Proben wiesen ausgeprägtere Mesoporen im Vergleich zu HTC auf, unabhängig vom Anteil des Ausgangsmaterials, was auf den Einfluss des Dampfes auf die Porenanordnung zurückzuführen ist. Während HTC signifikante organische Prozesswässer erzeugte, wurde durch den Zwei-Stufen HTC-Prozess eine weitere Reduktion erreicht, und VTC minimierte sie effektiv.

Die Produktion von aktivierter Kohle wurde durch HTC und ST untersucht. HTC-Bedingungen von 200 und 220 °C für 2 bzw. 4 Stunden, gefolgt von einer Aktivierung bei 650 °C, führten zu stark porösem Kohlenstoff. Ähnliche Ergebnisse wurden durch ST erzielt, ohne Vorbehandlung bei 750

°C, was zu einer höheren Porosität bis hin zu Makroporen und SSA führte. Der Vergleich zeigte, dass HTC aktivierten Kohlenstoff mit Mikroporosität produzierte, während ST Kohlenstoffe mit höherer Porenentwicklung und SSA erzeugte. HTC erzielte eine höhere SSA aus Hühnermist (488 m^2/g) im Vergleich zu ST (216 m^2/g), jedoch übertraf ST HTC in SSA aus Sägemehl (824 m^2/g gegenüber 660 m^2/g). Ein wesentlicher Nachteil von ST ist der vergleichsweise niedrige Ausbeuteanteil von 18 % im Vergleich zu 53 % bei HTC. Mit ST war es jedoch möglich, eine große Anzahl von Meso- und Makroporen mit Porenvolumina (PV) von 0,80 bzw. 6,40 cm^3/g zu erzeugen, während der Kohlenstoff, der durch HTC hergestellt wurde, hauptsächlich Mikroporen enthielt.

Die pyrolytische Karbonisierung (PYC) demonstrierte die Fähigkeit, aktivierten Kohlenstoff ähnlich wie ST zu erzeugen, mit marginalen Steigerungen der SSA und des Porenvolumens. PYC erreichte eine hohe Ausbeute von 83 %, was die niedrige Ausbeute von ST adressiert. Der aktivierten Kohlenstoff aus PYC zeigte ähnliche Porenstrukturen und SSA, was auf die Effektivität von PYC bei der Erzielung vergleichbarer Eigenschaften mit höheren Ausbeuten hinweist.

Anwendungen von aktiviertem Kohlenstoff in Natrium-Ionen-Batterien wurden untersucht. Die Kapazitätsergebnisse zeigten, dass Kohlenstoffelektroden aus ST und PYC mit höherer SSA und Mesoporen eine größere Kapazität von bis zu 128 mAh/g aufwiesen im Vergleich zur relativ geringen Kapazität, die aus HTC-Kohlenstoffelektroden im Bereich von 1 bis 4 mAh/g erzielt wurde. ST-Kohlenstoffelektrodenmaterial wurde auch mit industrieller Rußkohle verglichen und zeigte eine bessere Kapazität.

Das Potenzial von aktiviertem Kohlenstoff zur Wasserreinigung wurde durch Experimente zur Methylenblau-Absorption untersucht. Die Ergebnisse zeigten eine vollständige Farbstoffabsorption durch ST und PYC innerhalb von 60 Minuten, was auf eine überlegene Effizienz bei der Wasserreinigung im Vergleich zu HTC-abgeleiteten Kohlenstoffen hinweist, die nach 300 Minuten keine signifikante Absorption zeigten. Dies unterstreicht das Potenzial von aktiviertem Kohlenstoff mit hohen Meso-Makroporen, wie sie bei ST, PYC und VTC beobachtet werden, für Anwendungen in der Wasserbehandlung.

Diese Studie leistet erfolgreiche Pionierarbeit bei der Weiterentwicklung der Biowaste-Konversion durch verschiedene Carbonisierungsmethoden wie HTC, Zwei-Stufen HTC, VTC, ST und PYC. Der Fokus auf vielfältige Ausgangsstoffe, insbesondere Geflügelstreu (PL) bestehend aus Sägespänen und Hühnermist, eröffnet vielversprechende Möglichkeiten für die Produktion von chemischen Wertstoffen und die Synthese von Kohlenstoffmaterialien. Diese Erkenntnisse unterstreichen die Bedeutung methodischer Feinheiten und der Besonderheiten der Ausgangsstoffe, wobei VTC, ST und PYC als vielversprechende Kandidaten für Kohlenstoffmaterialien hervorgehen und die zweistufige HTC als effektives Werkzeug zur Optimierung der chemischen Ausbeuten und zur Minderung von Umweltbelastungen heraussticht. Die Produktion von Prozesswasser durch HTC unterstützt zudem das Algenwachstum, was zu einem nachhaltigeren Ansatz in der Abfallbehandlung beiträgt. Diese Forschung trägt zum wissenschaftlichen Verständnis der Carbonisierungsprozesse bei und befürwortet umweltfreundliche Technologien, mit dem Fokus auf Minimierung der Umweltbelastung und Maximierung der Ressourceneffizienz.

CERTIFICATION

I, Olayinka Ahmed Ibitowa, hereby declare that this research and the work presented in it is undertaken by me and have been generated as the results of my own original research. This work has not been presented elsewhere for the award of a degree or any other purpose.

Ibitowa OA.

Signature ………………………………………………………………

DEDICATION

This project is dedicated to Almighty God for His mercy and protection on us.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Preamble

In recent years, renewable and sustainable energy research has gained significant attention, particularly in countries striving to control and reduce carbon dioxide emissions (CO_2). This surge in interest has led to the establishment of numerous research centers and collaborations, working towards innovative solutions in the field (Friedrichs et al., 2020). The pressing need to address the global warming caused by fossil fuel products has promoted the research for alternative fuel sources.

Among the leading materials identified for minimizing CO_2 emissions and producing value-added products like biofuels and biochemicals, biomass and biowastes have emerged as promising contenders (McKendry, 2002). Through chemical and thermochemical synthesis, lignocellulosic biomass, a renewable and abundant resource, has shown potential as a substitute for fossil fuels in the sustainable production of specialty chemicals and transportation fuels (Nisha and Mohammed, 2005).

Lignocellulosic biomass encompasses various organic matters produced through photosynthesis and existing on the earth's surface (Nisha and Mohammad, 2005). It comprises of big trees, and above-ground biomass such as forestry, agricultural wastes, agro-industrial residues, and land-based vegetation. Additionally, it comprises municipal solid waste (MSW), such as municipal biosolids (sewage), animal waste (manures), and certain industrial waste, offering an abundant, renewable, and cost-effective energy (Chen et al., 2019).

Lignocelluloses, the constituents of biomass, consist of cellulose, hemicellulose, lignin, extractives, and inorganic materials (Sjostrom, 1993). Over the years, research has demonstrated that converting oxygen-functionalized biomass monomers (e.g., cellulose, hemicellulose) into value-added chemicals with low oxygen content is an effective approach (Yan et al., 2015). This strategy maximizes the utilization of lignocellulosic biomass, yielding cost-effective biofuels and platform chemicals that hold promise for sustainable fuel and commodity chemical production. Furthermore, lignocellulosic biomass can be used in the production of lightweight activated carbons (activated char), with applications in air, water and gas purification, soil amendment, catalyst support, chromatography, drug delivery, and energy storage (Titirici et al., 2015).

While various methods can be employed for the conversion of biomass for the production of chars and value-added chemicals such as 5-hydroxymethylfurfural (5-HMF), hydrothermal carbonization (HTC) has shown superior potential compared to pyrolysis, high-voltage arc discharge, chemical vapour deposition, and laser ablation (Basso et al., 2016) (Gonzalez et al., 2018).

HTC has garnered considerable interest in the field of renewable energy and biomass conversion due to its faster production of value-added chemicals, such as 5-HMF, and the generation of a coal-like char material termed hydrochar. This thermochemical treatment utilizes processing temperatures ranging from 120 to 250 °C and water as the carbonization medium under self-generated pressure (Titirici et al., 2012).

However, a notable drawback of hydrothermal carbonization technology is the generation of a relatively large amount of heavily polluted process water. To address this challenge, this research report explores the use of another carbonization technology which includes the vapour thermal carbonization (VTC), two-step (2-step) HTC, steam at elevated temperature (ST) and the pyrolytic carbonization (PYC). This research tests a system that uses superheated steam as compared to the saturated steam for the process. As a result, the feedwater obtained during HTC will be greatly throttled and thus, the amount of process water can be reduced. The actual carbonization would then be carried out in saturated steam, a process that must be balanced in accordance with the required saturated steam parameters (Li et al., 2017).

In this research report, a highly efficient method for converting biowastes to 5-HMF and activated char (carbon) is explored through the restructuring of cellulose using hydrothermal carbonization (HTC), 2-step HTC, steam at elevated temperature (ST), vapour thermal carbonization (VTC) and pyrolytic carbonization (PYC).

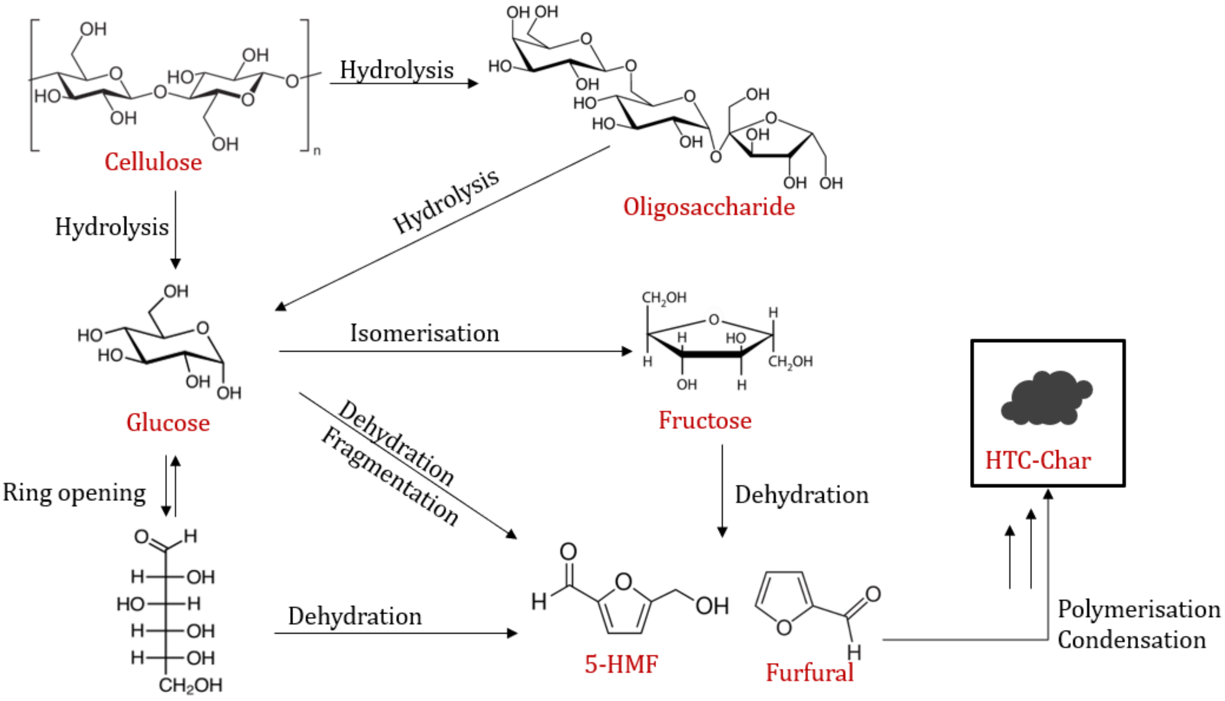

Figure 1: *Reaction Pathways for 5-HMF and char production T.Wang et al.,(2018)*

1.2 Statement of Problem

The European Union (EU) has witnessed a substantial surge in poultry meat production over the years, reaching an impressive figure of approximately 15.2 million tons in 2018 (Eurostat, 2018). This remarkable growth represents an increase of about one quarter or 3.2 million tons since 2010, highlighting the robustness of the poultry industry in the region. Among the EU member states contributing to this expansion, Germany stands out as the fifth-largest producer, accounting for 10.4% of the total poultry production.

The poultry industry in Germany is home to an extensive and thriving population of birds, including around 34 million layers, 60 million broilers, and 11 million turkeys, resulting in a cumulative total of approximately 105 million birds (BMEL, 2020).

However, with this soaring success in poultry production, there arises a pressing concern regarding the effective management of poultry litters consisting mainly of chicken manure and sawdust. Traditionally, poultry litters has been managed through land application as a means to enhance soil nutrients and act as a natural fertilizer, supporting agricultural productivity (Appels et al., 2010). Nevertheless, this convectional practice has led to several environmental challenges.

One of the major issues associated with conventional manure management is the potential for soil leaching, which occurs when excess nutrients from the manure infiltrate the soil and eventually reach surface and ground water, leading to environmental contamination (Jarvie et al., 2015). This contamination, especially with nitrogen and phosphorus, can cause detrimental effects on water quality, triggering eutrophication, and fostering the development of harmful algal blooms in water bodies (Howarth et al., 2011). Furthermore, the accumulation of excessive poultry litters, often stored in large quantities, can release offensive odors, posing nuisances to nearby communities and potentially affecting human health (Heathcote et al., 2015). Additionally, the high solubility of phosphorus and the rapid degradation rate of ammonium in poultry manure further contributes to nutrient loss and environmental pollution.

The negative consequences of improper poultry litter management, including its impact on air, water, and soil quality, have raised serious environmental and public health concerns. To address these challenges, the EU has implemented strict environmental legislation and regulations for farmers and agricultural industry in general, aiming to promote sustainable practices and mitigate the adverse effects of poultry litters disposal.

Considering these environmental and regulatory pressures, there is a growing need to explore innovative and sustainable manure management solutions. Rather than allowing poultry litters to become a potential pollutant, it could be harnessed as a valuable resource through the adoption of carbonization technologies (Cao et al., 2021).

Char derived from poultry litters has shown great potential in various applications, including soil amendment, as it can improve soil fertility, enhance water and nutrient retention, and sequester carbon (Lehmann et al., 2015). Additionally, the application of this char to agricultural soils can mitigate greenhouse gas emissions, reduce nutrient leaching, and promote sustainable agriculture practices (Mukherjee et al., 2014).

Furthermore, this char can also serve as a renewable energy source through the process of gasification, wherein it is converted into syngas, a mixture of carbon monoxide and hydrogen, which can be utilized for heat and power generation (Tian et al., 2016). This integration of char production and energy generation contributes to the circular bioeconomy concept, wherein waste materials are transformed into valuable resources, leading to greater resource efficiency and environmental sustainability (Hansen et al., 2020).

In conclusion, the exponential growth of the poultry industry in the EU, particularly in countries like Germany, has led to an increasing concern about the proper management of poultry litters. Traditional land application methods pose risks of environmental contamination and raise regulatory challenges. However, the adoption of carbonization technologies and the utilization of char production offer a promising avenue to convert poultry litters into a valuable resource that can improve soil quality, aid in air and water purification, reduce greenhouse gas emissions, and contribute to the sustainable bioeconomy.

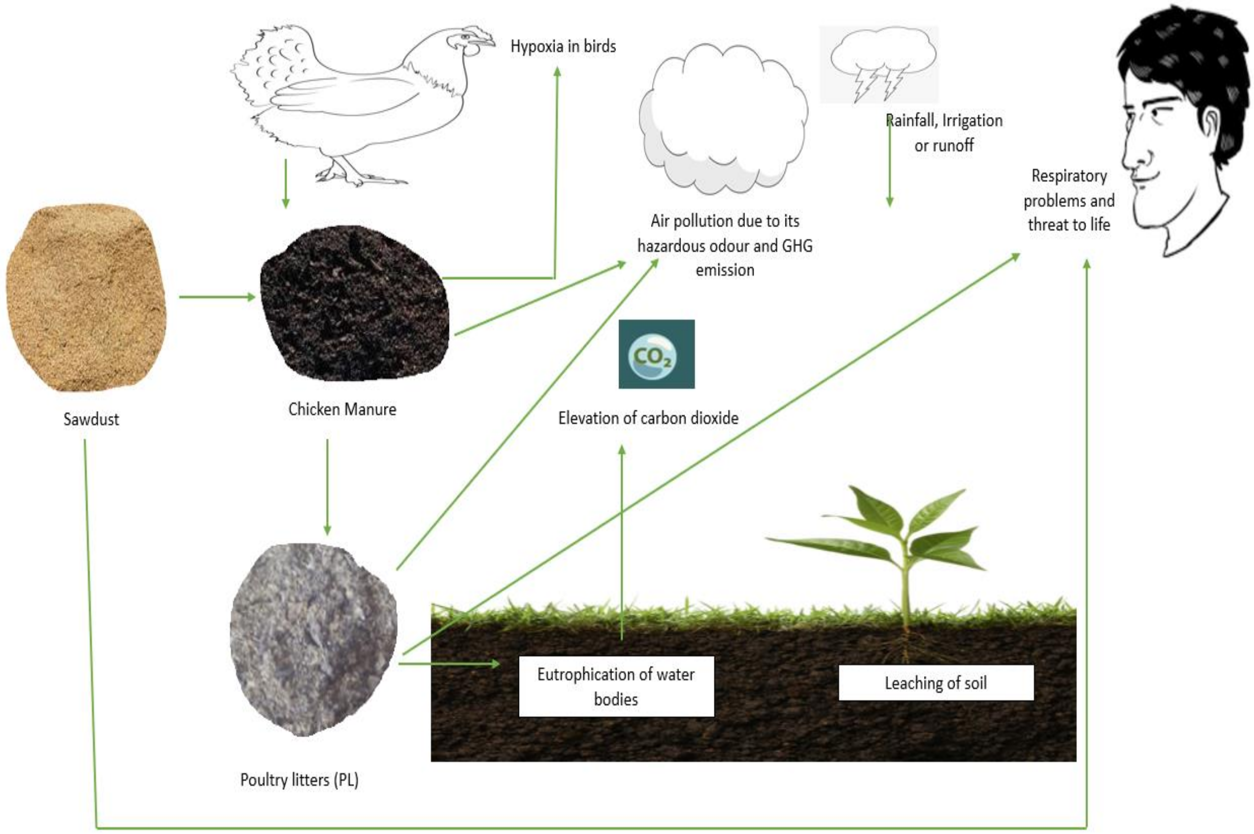

Figure 2: *Influence of PL on man and its environments*

1.3 Aim of the Research

The primary aim of this research is to develop an advanced waste-free technology for processing biowastes, specifically poultry litters consisting of sawdust and chicken manure mixed in different varied proportions, into high value-added products, e.g., 5-HMF and carbon materials (hydrochar) which will be further activated to produced activated char material.

1.4 Objectives of the Research

This research is designed with specific objectives to achieve the successful development and application of the waste-free technology for converting biowastes into valuable products. The key objectives are as follows:

i. Process development: Engineer processes that efficiently converts biowastes, into highly porous carbon.
ii. VTC-inlet design and fabrication: Design and fabricate a Vapour Thermal Carbonisation (VTC) inlet that can effectively perform carbonisation using vapour.
iii. High-throughput scale experiments: Conduct experiments on a high-throughput scale to optimize the formation of extractable value compounds, such as 5-HMF, from different mixtures of biowastes using the Two-step HTC.
iv. Impact of process water on algae cultivation: Investigate the influence of process water obtained from carbonisation especially HTC on algae cultivation, exploring potential applications in the context of sustainable algae-based processes and reduction of organic compounds in heavily process water.
v. Activated char formation and porosity: Perform lab-scale experiments using different biomass mixture and further physical activation to produce activated char with high porosity on different length scales, encompassing micro-, meso-, and macropores.
vi. Characterization: Thorough characterization of the hydrochars and activated char derived from carbonisation with a focus on chemical composition, porosity, and structural properties.

vii. Application Testing: Conduct testing and experimentation to explore the diverse applications of the activated char produced, investigating potential uses in environmental remediation, water purification or energy storage.

1.5 Justification

The significance of this research lies in addressing the pressing environmental and social challenges posed by poultry litters, a municipal solid waste. Improper management of poultry litters results in offensive odors and potential threats to human health, particularly in areas where it is stored. Moreover, its application to agricultural fields leads to the emission of high levels of nitrogen and phosphorus into the air and groundwater, contributing to environmental pollution and degradation. The improper disposal of this waste has caused severe environmental offenses in the EU, warranting urgent attention and sustainable solutions.

In Northern Germany, the sheer quantity of poultry litters presents a considerable waste management burden, prompting farmers to seek costly disposal options. The existing practices not only strain economic resources but also exacerbate environmental issues. However, this research proposes an alternative approach by harnessing the potential of poultry litters to create smart materials with diverse applications in various industries, such as supercapacitors and filter materials.

By converting poultry litters into valuable smart materials, this research aims to alleviate the negative impact of this waste on the environment and human well-being. Through innovative technologies and processes, this research was able to transform poutlry litters from a burden into a resource, thereby contributing to the principles of circular economy and sustainable waste management. The utilization of poultry litters as a precursor for smart materials presents numerous advantages. Firstly, it offers an eco-friendly and waste-free alternative for waste disposal, reducing the strain on landfills and lowering greenhouse gas emissions associated with traditional disposal methods. Secondly, the smart materials derived from poultry litters exhibit versatile properties that can be tailored for specific applications, fostering advancements in fields such as energy storage, water purification, and pollution control.

Ultimately, this research project contributed to the betterment of mankind and the environment by turning an environmental challenge into an opportunity for innovation and sustainable development. By transforming poultry litters into smart materials with valuable applications, the project aligns with the EU's environmental goals and facilitates the transition towards a cleaner, more resource-efficient future.

1.6 Scope of the Research

The scope of this research is to develop an innovative and sustainable waste-to-resource technology focusing on the production of valuable products; hydroxymethylfurfural (5-HMF) and activated carbon materials suitable for different applications. The technology will employ various carbonization techniques, such as vapourthermal carbonization (VTC), pyrolysis (PYC), two-step HTC (two-step HTC), and steam treatment or direct steam activation (ST) while comparing the output to the standard hydrothermal carbonization (HTC).

The research is limited to:

i. Production of 5-HMF: Focus on the development of an efficient and sustainable route for the production of 5-HMF. The objective is to obtain high yields of 5-HMF, a valuable platform chemical with multiple applications.
ii. Process design: design a new process for the conversion of poultry litters to useful carbenous materials.
iii. Generation of carbon materials for purification: Explore the production of carbon materials with tailored properties that are ideal for water and air purification applications. The carbon materials will be characterized by high specific surface area, porosity, and adsorption capacity, making them effective in removing pollutants from both liquid and gas phases.
iv. Characterization and analysis: Thoroughly characterize the carbon materials using advanced analytical techniques such as IR, XRD, SEM, BET, Hg intrusion and TGA.
v. Application testing: Test carbon materials for water and air purification applications, and for carbon electrode in Na-ion battery development.

1.7 Contribution to Knowledge

This research has significantly contributed to the field of waste-to-resource technology and environmantal sustianblility. The key contributions of the research are:

i. Advancement in carbonization techniques: The research explored and optimized multiple carbonization techniques, including the standard HTC, VTC, PYC, Two-step HTC, and ST, for the production of 5-HMF and carbon materials (activated carbon). The findings enhance the understanding of these processes, their efficiency, and potential applications, expanding the knowledge base in the area of biomass and waste conversion.

ii. Novel synthesis of 5-HMF: The development of an efficient and sustainable route for the production and optimization of 5-HMF from biomass feedstocks contributed to the advancement of green chemistry and renewable resources. This valuable platform chemical has broad applications, and its novel production method add to the existing body of knowledge in the field of bio-based chemicals.

iii. Tailored carbon materials: The research generated carbon materials with specific properties ranging from micro to macro pores optimized for water and air purification and application in Na-ion batteries.

iv. Comprehensive waste-to-resource system: By investigating the integration of various carbonization techniques, the research proposed a comprehensive waste-to-resource system that efficiently converts biowastes into high-value products. This holistic approach to waste management will offer a sustainable solution for both waste reduction and resource recovery.

v. Environmental and economic assessment: The life cycle assessment and economic analysis shed light on the environmental impacts and economic viability of the proposed technology. This knowledge will guide policymakers and industries towards more sustainable waste management practices and resource utilization.

vi. Application potential in water and air purification: Testing the synthesized carbon materials for water and air purification provided a valuable data on their efficiency and effectiveness in removing pollutants. These findings contributed to the development of sustainable and cost-effective solution for environmental remediation.

vii. Contribution to circular economy: The research aligns with the principles of circular economy by transforming waste into valuable resources. This contribution has inspired further reasearch and innovation in circular waste management strategies, enhancing the sustainability of various industries.

Overall, the research enrich the scientific community's understanding of waste valorization, renewable chemicals, and environmental applications of carbon materials. The knowledge generated have broad implications for sustainable development, poulltion control, and resource conservation, fostering a grenner and more resilient future.

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CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Waste-Free Technology Concept

The concept behind waste-free or zero-waste technologies seeks to fully utilize all parts of biomass feedstock while preventing the generation of waste during processing. Mohan et al. (2016) explained that "the waste-free biorefinery aims at 100 % valorization of biomass in a biorefinery concept without generating any waste. To maximize the value of renewable bioresources, there is a need to use the appropriate conversion processes. The idea of zero waste is consistent with circular economy models and green chemistry concepts (Cherubini, 2010). Valorizing every component of the biomass completes the material cycle and eliminates residues. Organic wastes serve as feedstocks for biofuels, platform chemicals, nutraceuticals, fibers, and carbon-based materials. Inorganic nutrients are recovered and recycled as fertilizers (Ahmed et al., 2019). Waste-free systems are designed to be self-sustaining, using internally generated process energy and co-products.

The development of waste-free biorefinery systems that maximize the valorization of all biomass fractions offers several important sustainability and economic advantages compared to conventional linear production systems. Waste-free processing would substantially reduce the environmental impacts associated with the landfilling, incineration or wastewater discharge of unused organic residues. Redirecting biowastes away from landfills would not only reduce greenhouse gas emissions resulting from anaerobic decomposition but also eliminate the potential risks of groundwater contamination. Incinerating waste biomass without harnessing energy is both environmentally inefficient and polluting. The discharge of dissolved organic matter into water bodies not only depletes oxygen levels but also inflicts harm upon aquatic ecosystems. Waste-free biorefineries offer significant environmental and public health advantages by removing the need for waste disposal (Isikgor & Becer, 2015). They also enable increased resource productivity and efficiency by getting the most economic value possible from renewable bioresources.

Chemicals, fuels, fibers, nutraceuticals, fertilizers and other products can be sustainably derived from all components of biomass, including lignocellulose, proteins, oils, and nutrients. This creates diverse revenue streams while regenerating organic matter and nutrients for agricultural application (Cherubini, 2010). Waste-free processing substantially improves the economic viability and profit margins of biorefineries by avoiding waste handling costs, which are substantial. Furthermore, utilizing waste carbon instead of fossil carbon translates into lower greenhouse gas impacts. The decentralized modular nature of waste-free systems allows them to be scaled down to accommodate localized residual biomass sources. This avoids high transportation costs as with centralized facilities (Pfaltzgraff et al., 2013).

2.2 Biowaste Feedstocks

Biowastes from agricultural, municipal, and industrial activities have grown exponentially due to rising populations, urbanization, and economic development (Mohan et al., 2016; Pfaltzgraff et al., 2013). These underutilized organic residues present unique opportunities and possibilities for conversion into renewable fuels, chemicals, and materials if appropriate technologies can be applied. A wide variety of biowastes are available, and their potential for waste-free valorization depends significantly on composition and properties (Binod et al., 2010). Agricultural residues constitute a large proportion of global biowaste. Lignocellulosic biomass in the form of crop residues, grasses, and forestry/wood wastes represents an abundant and renewable biowaste feedstock (Binod et al., 2010).

Global production of cereal straws alone is approximately 2 billion tons annually (Kronbergs, 2000). These materials contain cellulose (35 – 50 %), hemicellulose (20 – 35 %) and lignin (10 – 25 %), with minor amounts of extractives, ash, and protein (Isikgor & Becer, 2015). Lignin can provide a renewable source of aromatics, though its highly recalcitrant structure presents challenges (Linger et al., 2014). The rigid lignin binds cellulose and hemicellulose fibers, resisting rapid decomposition. The composition of lignocellulosic feedstocks varies with source material and local growth conditions, necessitating characterization before processing (Galbe & Wallberg, 2019; Galbe & Zacchi, 2007).

Animal manure is considered a highly significant biowaste, with approximately 60 million tons of dry harvestable manure generated annually from confined livestock and poultry operations. This substantial volume of manure results from the production of various manure byproducts (Priyadarsan et al., 2004). Animal manures are particularly rich sources of nitrogen, phosphorus, and potassium. According to Li et al., (2009), swine manure contains approximately 2.28 % N, 3.97 % P, and 2.09 % K on a dry weight basis. Nicholson et al. (1996) found that broiler/turkey litters had a higher dry matter content (around 60 %) compared to layer manures (around 35 %), but all manure types had similar concentrations of nutrients (N, P, K, Mg, S) on a dry weight basis. Ritz & Merka (2003) mentioned that the moisture content of chicken manure typically ranges from 20 to 40 %. The nutrient composition of manure can vary over time and is influenced by factors such as diet and management practices.

Despite making up a significant amount of biomass (18 %), animal manures have not been as well investigated as other plant-based feedstocks. The idea of feedstock from animal manures is current and well justified given the shift in animal husbandry toward concentrated animal feeding operations (CAFOs) over the last ten years. In many cases, the manure production from CAFOs exceeds the nutrient requirements of nearby pasturelands and nearby crops. The overuse of animal manure can cause eutrophication by causing the emergence of pathogens, the emission of ammonia, greenhouse gases, and odorous chemicals, as well as the enrichment of surface and ground waters with nitrogen and phosphorus compounds (Cantrell et al., 2007; Ro et al., 2007). A practical manure management approach that not only provides an environmentally acceptable manure treatment but also has the ability to generate income for farmers by manufacturing value-added biochar is carbonizing leftover animal manures from CAFOs.

Table 1: *Structural component of Lignocellulosic Biomass*

Component	**Features and Characteristics**	**References**
Cellulose	Linear homopolysaccharide of β-D-glucopyranose units bonded by β-1,4-glycosidic linkages	(Zhao et al., 2007; Sjöström, 1993)
	Degree of polymerization ranges from 800 to 10,000 units	(Klemm et al., 2005)
	Chains bundle together by hydrogen bonding and van der Waals forces forming crystalline microfibrils	(Nishiyama et al., 2002)
	Microfibrils provide tensile strength in plant cell walls	(Cosgrove, 2005)

	Hydrolyzes into glucose monomers by cellulase enzymes or dilute acids	(Mosier et al., 1999)
	Constitutes 35 – 50 % of lignocellulosic biomass	(Sun et al., 2002)
Hemicellulose	Heterogeneous polysaccharides based on C5 and C6 sugar monomers	(Scheller & Ulvskov, 2010)
	Includes xylans, xyloglucans, glucuronoxylans, arabinoxylans, mannans, glucomannans	(Ebringerová & Heinze, 2000)
	Branched and amorphous structure interlinks cellulose microfibrils	(Pauly & Keegstra, 2008)
	Easily hydrolyzed by dilute acid into pentoses and hexoses	(Mosier et al., 2005)
	Constitutes 20 – 35 % of lignocellulosic biomass	(Sun et al., 2016)
Lignin	Highly branched and heterogeneous aromatic polymer	(Boerjan et al., 2003)
	Derived mainly from three phenylpropanoid monomers: p-coumaryl, coniferyl and sinapyl alcohols	(Vanholme et al., 2010)
	Irregular polyphenolic structure resists chemical digestion	(Pu et al., 2011)
	Provides compressive strength, water impermeability and pest resistance	(Mottiar et al., 2016)
	Constitutes 10 – 25 % of lignocellulosic biomass	(Sun et al., 2002)

Thermal conversion of manure is challenged by high ash and moisture content, though flash pyrolysis and hydrothermal carbonization show promise (He et al., 2000; Kambo & Dutta, 2015). Extensive pretreatment and separation would likely be needed to optimize manure for waste-free valorization. Lignocellulosic residues and manures are particularly abundant at scale, however, the heterogeneous and variable nature of these wastes, as well as challenges in collection and transportation, constrain their utilization (Lin et al., 2013). Decentralized modular systems may be better suited to convert localized biowastes rather than centralized biorefineries

(Pfaltzgraff et al., 2013). Since different lignocellulosic materials have varying physio-chemical properties, it is vital to apply pretreatment procedures that are appropriate for each raw materials lignocellulosic biomass in order to increase digestibility and conversion efficiency. Additionally, the selection of a particular pretreatment has a significant influence on all subsequent phases in the total conversion scheme in terms of the digestibility of cellulose, the power needed for stirring, the amount of energy required in the downstream process, and the requirements for wastewater treatment (Galbe & Zacchi, 2007).

According to Su et al., (2015), treatment with alkaline hydrogen peroxide successfully removed lignin and hemicellulose from corncobs while essentially retaining the cellulose. To improve enzymatic hydrolysis, Sun et al., (2014) showed that a steam explosion pretreatment and alkaline delignification pairing effectively eliminated bamboo's hemicelluloses and lignin. Wang et al., (2013) studied the effects of lignin and hemicellulose removal on enzymatic hydrolysis and discovered that lignin played a dominating role in impeding the process. Bernal-Lugo et al., (2019) examined a one-step alkaline-organo-solvent pretreatment and demonstrated effective lignin and hemicellulose removal from softwood without cellulose loss. In addition, alkaline deep eutectic solvents (ADESs) can separate hemicelluloses from woody biomass, facilitating enzymatic hydrolysis (Yang, et al., 2021). Ma et al., (2021) examined a synergistic hydrothermal-DES pretreatment that enhances enzymatic saccharification by selectively dissociating hemicelluloses and removing lignin from poplar wood.

Wang et al., (2021) suggested a method for extracting hemicelluloses and high-purity lignin from moso-bamboo utilizing hydrothermal-DES pretreatment. According to Dong et al., (2019), functional acidic ionic liquids (ILs) can separate lignocelluloses into cellulose, lignin, and hemicelluloses. Ionic liquids can provide selective dissolution of lignocellulose with fractionation potential (Tan & MacFarlane, 2010). Steam explosion, liquid hot water, and ammonia fiber expansion (AFEX) alter structure and accessibility through thermal and chemical means (Alvira et al., 2010). Several pretreatment methods can be applied to lignocellulose to increase digestibility by altering structure and accessibility. Steam explosion, liquid hot water, and dilute acid hydrolysis remove and depolymerize hemicellulose, reduce cellulose crystallinity, and increase porosity (Alvira et al., 2010). Optimal pretreatment depends on the intended biowaste utilization pathway and economics.

Waste-free biowaste processing aims to utilize all components of the biomass feedstock and co-products, avoiding any waste generation. The waste-free concept is aligned with the principles of green chemistry and circular economy, with the goal of valorizing waste streams and enabling their re-introduction as raw materials into both biological and industrial production cycles. The thermochemical processes like pyrolysis, gasification, and hydrothermal liquefaction (HTL) use high temperatures to decompose biowastes. Hydrothermal liquefaction combines heat and pressure with an aqueous medium to convert wet biowastes like manure and algae into bio-crude oil (Toor et al., 2011). Gasification converts biomass into syngas ($CO + H_2$) through partial oxidation at high temperatures (800 – 1000 °C) enabling downstream fuel synthesis (Basu, 2010). Pyrolysis heats the feedstock in the absence of oxygen to produce char, bio-oil, and syngas products (Kambo & Dutta, 2015). Pyrolysis optimizes either biochar or bio-oil depending on heating rate and vapour residence time. Due to its established significance and use in the interdisciplinary fields of science and engineering, slow pyrolysis of biomass for the production of biochar, a stable carbon-rich solid by-product, has attracted significant interest. A relatively recent method termed hydrothermal carbonization (HTC) of biomass, which processes the biomass with hot compressed water rather than drying it, has shown promising results as an alternative for slow pyrolysis.

2.3 Pyrolysis

Pyrolysis is a prominent thermochemical conversion process used to convert solid biomass into liquid bio-oil, solid char and gaseous products. It involves heating the biomass in the absence of oxygen to temperatures typically between 300 – 600 °C. Pyrolysis enables the extraction of energy and value-added chemicals from renewable biomass in a sustainable manner. Based on the operating conditions, pyrolysis can be categorized into slow, intermediate, fast and flash pyrolysis. These are optimized to produce high yields of char, liquid or gas depending on the desired application. In slow pyrolysis, biomass is heated at slow heating rates of 5 – 20 °C/minutes and longer vapour residence times. Moderate temperatures around 400 – 550 °C are used along with longer reaction times of 5 – 30 minutes (Mohan et al., 2006).

The slow heating rates and longer residence times favour the production of solid char. The process yields 30 – 35 % char, 30 % bio-oil and 35 % gases on average (Tripathi et al., 2016). Slow pyrolysis is ideal for maximizing char production for applications like soil amendment and carbon sequestration (Manyà, 2012). Vakalis et al., (2017) explored thermochemical valorization of household biowaste and found that torrefaction and high-temperature pyrolysis produced biochar and other products with potential energy recovery.

The char retains most of the inorganic components of the original biomass. Its porous structure and high surface area make it suitable for adsorption applications. The bio-oil contains complex oxygenated hydrocarbons and water and requires extensive upgrading for fuel applications. The non-condensable gases like CO, CO_2, and CH_4 can be utilized for process heating requirements. The exothermic combustion reactions complement the endothermic pyrolysis reactions making the overall slow pyrolysis process self-sustaining. Slow pyrolysis is the traditional method used for charcoal production. Furthermore, in fast pyrolysis, fine biomass particles are rapidly heated to moderate temperatures of around 500 °C with short vapour residence times of 0.5 – 2 seconds (Mašek, 2016; Bridgwater, 2012). High heating rates of up to 1000 °C/s are employed. Short residence times and rapid quenching minimize secondary reactions enabling higher liquid yields (Ibrahim, 2020). Fast pyrolysis yields 60 – 75 % bio-oil, 15 – 25 % char and 10 – 20 % non-condensable gases (Jiang et al., 2016; Czernik & Bridgwater, 2004). It is ideal for maximizing bio-oil production which can be used as a substitute for fuel oil or a source of specialty chemicals after substantial upgrading (Mohan et al., 2006).

The bio-oil is made up of highly oxygenated organics like phenols, ketones, esters, sugars, furans and organic acids along with 20 – 30 % water content (Oasmaa & Czernik, 1999). The moisture content leads to a lower heating value of around 16 – 19 MJ/kg compared to 40 MJ/kg for conventional fuel oil (Bridgwater et al., 1999). The bio-oil is acidic with a pH of 2 - 3. It is immiscible with conventional petroleum fuels. These issues necessitate significant catalytic upgrading to remove oxygen and enable fuel-grade bio-oil production. The char is of limited value due to low yields. Fast pyrolysis is the preferred option when bio-oil for refinery applications is the desired target product.

Moreover, flash pyrolysis employs extremely high heating rates greater than 1000 °C/s and very short vapour residence times of < 0.5 sec. Biomass particles < 1 mm in size are used along with fluidized bed reactors that provide excellent heat transfer (Mohan et al., 2006). The ultra-high heating rates and short contact times maximize liquid bio-oil yields up to 80 % (Bridgwater et al., 1999). Gas yields are 5 – 10 %. Flash pyrolysis is suitable only for small-scale analytical studies due to the technical challenges and high energy intensity of these extreme operating conditions (Vamvuka, 2011). Nonetheless, intermediate pyrolysis covers a wide range of heating rates, temperatures of around 500 °C and vapour residence times between fast and slow pyrolysis (Brown, 2011). It provides more flexibility in varying product distributions favoring either biochar or bio-oil depending on needs. It is also less energy-intensive compared to fast pyrolysis. Heating rates of 10 – 200 °C/minutes and residence times of 0.5 – 10 sec can be employed with average product yields of 50 % liquid, 30 % solid and 20 % gas (Heo et al., 2010). The wide operating window of intermediate pyrolysis enables optimizing conditions based on feedstock type and required application of the products.

A variety of pyrolysis reactor systems have been developed to provide a range of operating conditions suitable for slow, fast and flash regimes. Fixed bed reactors are simple and inexpensive. The biomass moves through the reactor by gravity as it gets thermally decomposed. They are suitable for slow pyrolysis producing mostly char. Fluidized bed reactors employ inert bed materials that maintain excellent heat transfer to the biomass. They can provide the rapid heating and heat transfer rates needed for fast pyrolysis bio-oil production (Bridgwater & Peacocke, 2000). Rotating cone and ablative reactors also enable very high heating rates and are specially designed for flash pyrolysis conditions. Microwave and plasma-assisted pyrolysis methods are emerging that use electromagnetic or plasma energy to provide rapid biomass heating (Chew & Doshi, 2011). Continuous screw-type auger reactors move the biomass through the heated unit continuously. Intermediate pyrolysis conditions can be attained using all these reactor configurations by controlling the biomass feeding rate, vapour residence time and quenching rate.

2.3.1 Effect of Operating Conditions on pyrolysis

2.3.1.1 Temperature

Pyrolysis temperature has a major effect on product distributions. At lower temperatures of 300 - 400 °C, solid char formation is favoured due to mild heating that results in the release of lightweight volatile compounds. As temperature rises to 600 °C, vapours reside longer enabling thermal cracking into smaller organics that condense into bio-oil. Very high temperatures beyond 800 °C result in secondary gas phase cracking reactions producing high gas yields (Yang et al., 2007). Longer vapour residence times also enable secondary thermal cracking boosting gas yields. Pyrolysis temperature has a significant effect on the properties and yields of pyrolysis products including biochar, bio-oil, and syngas. According to Cantrell et al. (2012), as pyrolysis temperature increases, biochar yield decreases due to more decomposition of the biomass, leaving less solid carbonaceous material. Boateng et al. (2007) found that bio-oil yield initially increases with temperature and then decreases at higher temperatures as more vapours are converted to permanent gases. The yield of non-condensable syngas was observed by Boateng et al. (2006) to increase with pyrolysis temperature as secondary decomposition reactions produced more permanent gases like CO, CO_2, and CH_4 instead of condensable vapours. Cantrell et al. (2012) showed that the carbon content of biochar decreases as temperature increases because more carbon is converted to gaseous form. Qian et al. (2013) demonstrated that biochar surface area increases with temperature due to the removal of volatile matter and the development of porosity, up to a point where excessively high temperatures can lead to pore collapse.

According to Cantrell et al. (2012), biochar ash content increases with temperature since most ash components do not volatilize during pyrolysis. Boateng et al. (2006) found that bio-oil water content decreases at higher temperatures due to dehydration reactions. The energy density of bio-oil was shown by Boateng et al. (2007) to initially increase with moderate pyrolysis temperatures around 500 °C but then decline at excessively high temperatures when the high gas yield lowered the condensable liquid energy density. In summary, research shows that moderate pyrolysis temperatures around 500°C optimize bio-oil yields and quality, while lower temperatures around 350 – 400 °C favour biochar production. Pyrolysis temperature is an important parameter that can be optimized based on the desired end product.

2.3.1.2 Feedstock

The choice of biomass feedstock has a significant impact on the properties and yields of pyrolysis products. According to Qian et al. (2013), feedstocks can range from agricultural residues to forestry residues, wood, municipal solid waste, and animal manures. Boateng et al. (2006) tested switchgrass, oak, and pine wood, finding that the inherent properties of the feedstock including mineral content, elemental composition, and fiber structure influence the qualities of the resulting biochar, bio-oil, and syngas. Feedstocks with high moisture absorb heat for water evaporation resulting in lower pyrolysis efficiencies. Smaller particle sizes enhance heat transfer and product yields. Catalysts like zeolites and metals can optimize bio-oil quality (Stefanidis et al., 2011). Cantrell et al. (2012) pyrolyzed dairy manure, turkey litter, swine solids, poultry litter, and feedlot manure, observing differences in biochar pH, surface area, carbon content, energy density, and mineral concentrations attributable to variations in feedstock. Brewer et al. (2009) found that biochars derived from corn stover and rye had higher mineralization rates compared to pine wood biochar, likely due to differences in original feedstock composition.

Some general trends have been noted with woody versus herbaceous feedstocks. Woody feedstocks produce biochars with higher surface area and porosity compared to herbs (Qian et al., 2013). Herbaceous feedstocks yield biochars with greater mineral and alkali contents (Cantrell et al., 2012). Woody feedstocks generate biochars that are less prone to microbial degradation compared to grasses (Brewer et al., 2009). Feedstocks high in lignin, cellulose, and hemicellulose increase bio-oil production compared to high ash/mineral feedstocks (Boateng et al., 2006). However, research has demonstrated that feedstock selection significantly influences the products and properties of pyrolysis through inherent compositional variations. Optimization of feedstock is important in either the production biochar or bio-oil as the main product.

2.3.1.3 Heating rates

Heating time, also referred to as residence time, impacts biomass pyrolysis product yields and properties. According to Boateng et al. (2007), typical heating times range from seconds to hours depending on the pyrolysis technique, with fast pyrolysis favoring shorter times on the order of seconds to maximize bio-oil production. Cantrell et al. (2012) used relatively long heating times of 60 - 120 minutes to produce biochar, reflecting a slow pyrolysis process. Heating rates dictate bio-oil versus char yields. Slow rates allow enough reaction time for conversion into solid char. Very fast heating rates 'freeze' the decomposition rapidly into volatile vapours minimizing char formation. Biomass with higher lignin content produces more bio-oil while high cellulose feedstocks favor solid char (Mullen et al., 2010).

With increasing heating time at a constant temperature, biochar yield increases initially and then levels off as shorter heating times may not allow for full decomposition and carbonization while longer heating times favor increased solid char production up to an optimal point (Cantrell et al., 2012). Bio-oil yield decreases with longer heating times as secondary reactions convert more vapours into non-condensable gases; shorter heating times around 1 second maximize bio-oil production in fast pyrolysis (Boateng et al., 2007). Non-condensable gases increase with longer heating times as secondary decomposition reactions have more time to produce permanent gases (Boateng et al., 2007).

Additionally, biochar carbon content increases initially as short heating times can produce incompletely carbonized biochar while longer times allow more decomposition to produce higher carbon biochar (Cantrell et al., 2012). Biochar surface area also increases initially as more time allows volatile matter to be removed, developing porosity up to an optimal point (Cantrell et al., 2012). Therefore, slow fast pyrolysis heating times favour bio-oil production, while slow pyrolysis with longer heating times on the order of hours is optimal for producing high-carbon, porous biochar.

2.3.2 Physicochemical Characteristics of the pyrolysis products

The biomass pyrolysis products have distinct characteristics. The pyrolysis bio-oil is a dark brown, free-flowing liquid. It is chemically very complex containing over 400 identified compounds like acids, alcohols, aldehydes, ketones, phenols, ethers, esters and saccharides along with high oxygen levels of 35-40%. Water makes up 15-30% giving it a low pH of 2 - 3. It has an average higher heating value of 16-19 MJ/kg, viscosity of 40-100 cP at 40 °C and density of 1.05 - 1.25 g/ml (Zhu, 2016; Oasmaa et al., 2003).

The pyrolysis char is a solid carbonaceous material containing 85 – 95 % fixed carbon and 5 – 15 % ash. It has high porosity and a surface area of 150 - 400 m^2/g. The heating value ranges from 28 – 35 MJ/kg depending on process conditions. The non-condensable gases consist primarily of CO, CO_2, CH_4, H_2, and C_2 - C_6 hydrocarbons and have medium heating values of around 12 – 20 MJ/m^3 (Jahirul et al., 2012).

2.4 Gasification

Gasification is a prominent thermochemical conversion process used to convert solid biomass into a combustible gas mixture called syngas. It involves reacting the biomass at high temperatures >700 °C with a controlled amount of oxygen and/or steam. Gasification enables extracting energy and valuable chemicals from renewable biomass in a sustainable manner. Based on the gasifying media used, gasification can be classified into air, oxygen, steam or hydrogasification.

In air gasification, biomass is partially oxidized at 800 – 1000 °C using air as the gasifying agent. The oxidizing environment facilitates exothermic combustion reactions between biomass and oxygen generating heat for the process (Basu, 2018). Typical air-to-biomass ratios range from 0.2 - 0.5 kg/kg. The syngas produced have a low calorific value of around 4 – 7 MJ/Nm^3 and is composed primarily of N_2, CO_2, CO, H_2 and CH_4 (Zeng et al., 2015) High N_2 dilution from the air lowers the syngas quality. Significant tar and soot are also produced due to low temperatures. The gas requires extensive cleanup before utilization in engines or turbines for heat and power generation. Air gasification is the simplest and cheapest option but produces poor-quality syngas unsuitable for chemical synthesis (Ruiz et al., 2013) In addition, the use of high-purity oxygen instead of air for gasification improves syngas quality by eliminating N_2 dilution. High oxygen-to-biomass ratios above 0.5 are used at temperatures 900 – 1000 °C (Ma et al., 2016). This enriched oxidizing environment ensures complete carbon conversion and tar breakdown. Although energy intensive, this enables the production of syngas with medium calorific values of 10-18 MJ/Nm^3 containing CO, H2 and CH_4 as main constituents (Higman & Burgt, 2008). The higher temperatures enhance tar cracking and shift reactions improving CO and H_2 yields. Oxygen gasification requires costly air separation units but enables superior syngas quality compared to air gasification, suitable for power generation and chemicals/fuels synthesis via Fischer-Tropsch (He et al., 2010).

Nonetheless, steam gasification employs steam as the gasifying agent instead of oxygen. Biomass is reacted with steam at 750 – 1000 °C at near atmospheric pressure using steam to biomass ratios of 0.5 – 3 kg/kg (Miccio et al., 2021). The high-temperature steam serves as a source of H_2 and the oxidant facilitating predominantly endothermic steam reforming reactions with biomass. This produces syngas with very high hydrogen content and high calorific value of 10 – 20 MJ/Nm3 containing mainly H_2, CO, CO_2 and CH_4 (Kundu et al., 2021). However, a large heat input is needed to maintain the high temperatures required for sufficient steam production and tar breakdown. Operating cost is increased but a very high-quality syngas suitable for chemicals and fuels synthesis is obtained via steam gasification.

Hydrogasification uses H_2 instead of steam as the gasifying agent for biomass. Typical hydrogasification conditions are 300 – 350 °C temperature and 5 – 10 MPa pressure with H_2 to biomass ratios of 0.5 – 2 kg/kg (Sutton et al., 2021). The low process severity minimizes tar formation. Hydrogenation reactions dominate producing clean syngas with very high heating values of 35 – 45 MJ/Nm^3 and H_2 content above 60 % (Sikarwar et al., 2016). Moreover, providing high-purity H_2 significantly increases operating costs. Overall, hydrogasification generates the best quality syngas for fuel and chemical production with minimal contaminants. However, the need for external H_2 supply makes the process economically prohibitive currently (van Rossum et al., 2007).

2.4.1 Effect of Process Conditions on Gasification

Temperature has the most significant impact on gasification performance. High temperatures of 800 – 900 °C are needed to obtain complete gasification efficiency and desired syngas composition. Low temperatures favor tar and char generation while very high >1000 °C temperatures accelerate soot formation (Coll et al., 2001). Gasifying agents like steam and oxygen influence syngas composition while pressure and feed characteristics like moisture and ash content impact process energetics and efficiency.

Catalysts such as dolomites, nickel, zeolites etc. can be used to promote tar cracking and reforming reactions enhancing H_2 production (Stemmler et al., 2014). Feed characteristics like high moisture require heat for drying which lowers efficiency. Gasifying agents dictate oxidizing versus non-oxidizing conditions significantly affecting syngas composition. Thus, optimizing process parameters is vital to maximizing syngas yield and tailored composition.

2.4.2 Syngas Composition

Syngas composition is the most important characteristic dictating potential applications. Air gasification produces syngas with 15 – 20 % CO, 10 – 15 % H_2, 1 – 5 % CH_4 and 50 – 55 % N_2. Oxygen gasification generates syngas with 35 – 45 % CO, 25 – 35 % H_2, 5 – 15 % CO_2, 5 – 10 % CH_4. Steam gasification syngas has 20 – 30 % H_2, 15 – 25 % CO, 10 – 15 % CO_2, 5 – 10 % CH_4. Hydrogasification syngas contains 60 – 70 % H_2, 15 – 20 % CO, 5 – 10 % CO_2 (Basu, 2010). Air and oxygen syngas are suitable for power generation in gas engines and turbines. Steam and hydrogasification syngas can serve as feedstock for Fischer-Tropsch fuels and chemical synthesis after additional conditioning.

Table 2: *Summary of thermal processes and its key differences*

Process	Feedstock	Temperature	Pressure	Main Products	Key Differences	References
Pyrolysis	Solid biomass with <10 % moisture	300 – 1000 °C	Atmospheric or vacuum	Biochar, bio-oil, syngas	The thermochemical process occurs in the absence of oxygen. Optimized for biochar or bio-oil production.	Kambo & Dutta, 2015; Li et al., 2013; Basu, 2010
Gasification	Solid biomass with	>700 °C	Atmospheric or pressurized	Syngas (CO + H_2)	Partial oxidation of biomass creates syngas. High	Basu, 2010; Puig-Arnavat et al., 2010

	<15 % moisture				temperatures promote tar cracking.	
Hydrothermal carbonization (HTC)	High-moisture biomass slurries	180 – 250 °C	Self-generated	Hydrochar	Wet carbonization in closed system at moderate temperatures maximizes solid hydrochar yield.	Hu et al., 2022; Arauzo et al., 2018; Liu et al., 2013; Libra et al., 2011

2.5 Carbonization Technology

2.5.1 Hydrothermal Carbonization (HTC)

Hydrothermal carbonization (HTC) is an emerging thermochemical conversion process that can convert wet biomass feedstocks into a coal-like material called hydrochar. Unlike other thermal conversion processes like pyrolysis and gasification which require drying the feedstock, It involves treating biomass in hot compressed water at temperatures 180 – 350 °C and autogenous pressures, making it an energy-efficient approach (Hu et al., 2022; Arauzo et al., 2018; Liu et al., 2013; Libra et al., 2011). At these supercritical water conditions, the biomass components undergo hydrolysis, depolymerization and repolymerization reactions to form a complex oil-like liquid product (Lopez et al., 2018). The process parameters including reaction temperature, residence time, feedstock loading and catalysts have significant effects on the yield and properties of hydrochar. In terms of process cost and performance efficiency, the HTC process has a number of advantages over conventional dry-thermal pre-treatments such as slow pyrolysis, particularly its capacity to process wet feedstock without the need for pre-drying (Kambo & Dutta, 2015).

Lee et al. (2019) found that HTC of leather waste produced hydrochar with a higher heating value compared to low-ranked coals, making it a suitable alternative fuel. Similarly, Yu et al. (2018) reported an increase in the higher heating value of hydrochar produced from anaerobic granular sludge with increasing HTC temperature. However, Peng & Liu (2015) and Gao et al. (2016) both found that HTC of waste biomass resulted in hydrochars with improved fuel qualities, including increased energy density and reduced pollutant emissions. Hydrothermal carbonization (HTC) is a promising process for the conversion of biomass to valuable chemicals, however, further studies are needed to address the challenges associated with its carbon losses and energy requirements (Funke et al., 2013).

2.5.2 Vapourthermal carbonization (VTC)

Vapourthermal carbonization (VTC) is a thermochemical conversion process that has been developed from hydrothermal carbonization (HTC) which uses vapour as a means of its thermochemical treatment. Both processes use heat and pressure to mimic natural coalification and produce a solid fuel known as hydrochar or biochar from biomass feedstocks in a much shorter timeframe than the millions of years required to form fossil coal (Shafie et al., 2018; Funke & Ziegler, 2010).

Both hydrothermal carbonization (HTC) and vapourthermal carbonization (VTC) are two methods for converting wet biomass into energy-dense solid products. HTC, which involves exposing wet biomass to hot, pressurized water, has been shown to increase the energy density of the resulting char (Hoekman, 2011). The biomass feedstock is fully submerged in liquid water and heated under pressure, typically between 180 – 250 °C for 0.5 – 12 hours (Kambo & Dutta, 2015). VTC, on the other hand, uses saturated steam (vapour) instead of liquid water, resulting in higher process efficiency due to reduced carbon losses and lower water requirements (Funke et al., 2013). Water vapour plasma technology has also been explored for biomass conversion, with the potential to produce synthetic gas (Grigaitienė, 2011). Additionally, the VRC (vapour recompression) dehydrator, a type of energy-efficient dryer, has been proposed for use in the dehydration of wet biomass, potentially leading to increased electricity generation compared to anaerobic digestion (Hino, 2005). Some of the key differences if not all will affect process management, plant costs and design, feedstock requirements, and product characteristics of these thermal processes.

2.5.3 Comparative analysis of VTC and HTC processes

A key advantage of VTC is simpler process management compared to HTC. Vapour Thermal Carbonization (VTC) offers simpler process management compared to Hydrothermal Carbonization (HTC) due to its higher solid content in the reactor, lower carbon losses in the liquid phase, and reduced water heating requirements (Funke et al., 2013). However, both VTC and HTC have their advantages and challenges, with HTC being a potentially green method for deconstructing biomass into platform chemicals or energy carriers (Lachos-Perez et al., 2021). HTC also has the potential to produce a variety of cheap and sustainable carbonaceous materials with attractive nanostructure and functionalization patterns (Titirici & Antonietti 2010). Despite these advantages, VTC's simpler process management makes it a promising alternative to HTC for biomass carbonization.

Hydrothermal carbonization (HTC) and vapour-based hydrothermal carbonization (VTC) are both thermochemical processes, but they differ in their operation parameters and technical issues (Lachos-Perez et al., 2021, Ro 2020). HTC involves the use of high-pressure hot slurries, while VTC involves vapour and vapour condensation, similar to other thermochemical processes like torrefaction (Lachos-Perez et al., 2021, Ro et al., 2020, Funke & Ziegler, 2010). The byproduct of the HTC process often contains high levels of total organic carbon and toxic organic compounds, necessitating further treatment (Reza et al., 2016). The HTC process can produce gaseous and water-soluble products, water, and a solid char, with the energy density of the char increasing with reaction severity (Hoekman et al., 2011).

An advantage of VTC is that feedstocks do not require size reduction or drying before carbonization. Literature suggests biomass can be used in VTC systems without any pretreatment, unlike HTC which requires an energy-intensive size reduction step to create a pumpable slurry (Ro et al., 2020; Funke & Ziegler, 2010). Eliminating feedstock preprocessing and simplifying reactor designs indicates that VTC could achieve higher throughputs and lower capital costs. However, sufficient contact between steam and biomass must still be ensured, for example by using perforated reactors and mixing as demonstrated up to pilot-scale volumes of 4.6 litres (Shafie et al., 2018).

In terms of combustion behaviour relevant to solid fuel applications, VTC chars were found to have higher ignition temperatures and stabilities (Shafie et al., 2018). However, HTC hydrochars demonstrated more consistent mass loss and heat production in TGA analysis, indicating perhaps more predictable performance in boilers (Minaret & Dutta, 2016). Ultimately, hydrochars produced via HTC and VTC do not significantly differ and both achieve the primary goal of increasing carbon content and energy density 2 – 4 fold compared to the original biomass (Kambo & Dutta, 2015). More research is needed under consistent reactor conditions to compare outcomes.

In HTC, dissolved organics and inorganics can concentrate over successive batches into a corrosive acidic liquid requiring wastewater treatment before disposal or reuse (Stemann et al., 2013). However, HTC wastewater may contain valuable biomethane potential for biogas production (Heidari et al., 2019). In comparison, steam condensate generated in VTC has received little characterization but may contain fewer dissolved organics without direct submersion in liquid water. This condensate likely still requires neutralization but has been successfully recycled to generate steam without reported issues (Funke & Ziegler, 2010; Shafie et al., 2018).

Hydrothermal carbonization (HTC) and vapourthermal carbonization (VTC) refer to thermochemical conversion techniques used to process biomass and organic waste feedstocks into value-added carbonaceous materials referred to as hydrochars. The techniques utilize hot compressed water or steam to initiate a series of reactions that partially decompose and carbonize the feedstock into a coal-like product (Libra et al., 2011). With increasing attention to renewable energy sources and sustainable waste management practices, HTC and VTC have gained interest in producing hydrochar that can serve as a solid fuel or soil amendment. Although the two hydrothermal processes have similarities, several important differences between HTC and VTC have been reported in the literature.

The foremost difference lies in how the feedstock initially contacts water at the start of the hydrothermal reaction. In conventional HTC systems, the feedstock particles are fully submerged within a liquid water phase inside the reactor vessel from the outset (Cao et al., 2013; Funke et al., 2013). The feedstocks are typically dried materials mixed with a specified mass of liquid water before reactor loading. In contrast, VTC configurations suspend the feedstock particles in baskets or trays inside the reactor so direct contact with bulk liquid water is intentionally avoided (Yeoh et al., 2018; Shafie et al., 2018). VTC feedstocks often have some innate moisture content or are prewetted, but remain physically apart from any additional liquid water pooled in the bottom of the reactor system. Hence, vapourthermal reactions initiate solely between the feedstock and vapour phase steam during the heat-up phase rather than liquid water in HTC systems.

2.5.4 Process Conditions Over Reaction Timeline

The distribution of water between the vapour and liquid phases progressively changes with increasing temperature and pressure for both HTC and VTC reactions. As steam condenses to liquid, the accumulated condensate comes into contact with and penetrates the suspended feedstock particles in VTC systems (Ro et al., 2020). Hydrothermal carbonization reactions can then occur between the feedstock and adsorbed water. Similarly, accumulating reaction intermediates and products dissolved in the liquid phase also diffuse into the solid matrix over time in both HTC and VTC processes. Nevertheless, the level of exposure to liquid water contact throughout the full reaction period markedly differs between HTC and VTC configurations.

In conventional HTC, the feedstock particles remain fully immersed in bulk liquid water for the hydrothermal reaction hold time. Experimental measurements and theoretical models presented by Ro et al. (2020) suggest the volume fraction of liquid water (VFw) in HTC reactors can increase as temperature ramps up. This occurs because density reductions with heating cause volume expansion that is accommodated within the fixed reactor volume. The heightened exposure to liquid water facilitates increased hydrothermal carbonization reactions compared to VTC (Cao et al., 2013).

By comparison, VTC systems purposefully limit feedstock contact with any liquid water that condenses from the steam phase over time or otherwise accumulates in the reactor by design. Suspended feedstocks and continual condensate drainage avoids feedstock penetration into bulk liquid water that preferentially pools at the reactor bottom (Shafie et al., 2018). Exposure remains limited to adsorbed condensed moisture on particle exteriors. Consequently, hydrothermal carbonization reactions occur but develop to lesser extents in VTC based on the restricted liquid water reactions, particularly relative to submerged HTC feedstock (Funke et al., 2013).

Researchers suggest VTC products retain a portion of aliphatic compounds not destroyed during the milder hydrothermal processing induced by limited liquid water exposure (Funke et al., 2013). As such, heating values of VTC hydrochar can suffer somewhat compared to HTC generated analogues while biodegradability prevails to a greater extent. The few direct HTC versus VTC comparisons do demonstrate VTC achieves significantly higher hydrochar yields than submerged HTC techniques, likely a result of heightened solubilization and secondary decomposition reactions in HTC processes (Yeoh et al., 2018). From the process efficiency standpoint though, superior VTC yields can offset slightly reduced heating values to give enhanced energy and carbon recovery relative to conventional HTC based on existing data (Shafie et al., 2018).

2.5.5 Challenges of HTC and VTC

The upgrading of wet biomass sources into solid fuel char presents challenges when using conventional thermal carbonization methods. Hydrothermal carbonization (HTC) and vapourthermal carbonization (VTC) allow direct wet biomass carbonization. However, several key challenges remain for the commercial-scale implementation of these technologies (Shafie et al., 2018; Funke & Ziegler, 2010). Nearly all the HTC and VTC reactors are batch systems (Tekin et al., 2014; Funke & Ziegler, 2010), limiting production capacity for industrial viability. Developing continuous HTC/VTC processes requires overcoming substantial technical and cost hurdles in materials, design, and process control to sustain the required high temperature and pressure conditions (Tekin et al., 2014). Attempts using modified twin screw extruders as continuous HTC reactors have shown issues matching batch reactor fuel quality (Mäkelä et al., 2016). The batch production method also hinders integration with upstream and downstream process operations (Tekin et al., 2014).

Both HTC/VTC are emerging thermal conversion processes for wet waste conversion into valuable chemicals. However, as Kasiuliene et al. (2019) found, treating of biomass and biowaste via HTC generate process water requiring further management or treatment. Up to 36 % of the initial sorbent mass was transferred to the liquid phase as dissolved organic carbon (7038 – 7558 mg/L). Additionally, the process water accumulated significant concentrations of contaminants like arsenic, copper, and zinc leached from the original sorbent (Kasiuliene et al., 2019). For example, approximately 62 % of the adsorbed arsenic is released into the process water after HTC of the raw peat sorbent. Direct discharge of such streams could allow the re-mobilization of toxic elements in the environment. The contaminated process waters had high COD loads alongside metalloid presence exceeding safe limits, similar to challenges noted for conventional thermal process waters by Sharma et al. (2022) and Xiong et al., 2019. While Kasiuliene et al. (2019) suggest chemical precipitation post-treatment, developing lower-cost solutions remains an active research need.

Treating the acidic wastewater and condensate byproducts from HTC/VTC is another significant challenge (Shafie et al., 2018; Kambo & Dutta, 2015). Direct discharge of these effluents risks environmental damage while implementing treatment systems adds complexity and costs to the processes. Water recycling has benefits but can allow a buildup of inhibitory contaminants that undermine process performance over multiple reuse cycles (Stemann et al., 2013). While the HTC/VTC fuel product has improved properties like higher heating value compared to raw biomass, the mass yield is considerably reduced due to devolatilization reactions (Shafie et al., 2018; Kambo & Dutta, 2015). The lower mass yields could mean reduced overall energy yields and viability thresholds for commercial production (Tran et al., 2017). There are also quality consistency issues meeting specifications for end uses like co-firing (Kambo & Dutta, 2015). Feedstock variability paired with fluctuations in process conditions leads to significant variability in product fuel properties that needs further study (Kambo & Dutta, 2015).

Additional R&D efforts are necessary to engineer durable HTC/VTC reactor and process equipment designs (Kambo & Dutta, 2015; Tekin et al., 2014). Preventing corrosion and metallic contamination while managing solids deposition and fouling from intermediates for sustained, efficient operations remains a key materials challenge (Kambo & Dutta, 2015). Techniques for efficiently dewatering the hydrophilic hydrochar product also need refinement (Kambo & Dutta, 2015). Thermal drying of the products to remove bound moisture is highly energy-intensive (Shafie et al., 2018). While lab investigations demonstrate HTC/VTC fuel property improvements, scaling these reactions introduces heat and mass transfer considerations along with uncertainties in translating the kinetics and efficiencies to larger reactors and process configurations (Kambo

& Dutta, 2015; Yoshikawa, 2009). Rigorous techno-economic analyses are lacking at pre-commercial scales (Tekin et al., 2014).

If HTC/VTC facilities are sited near biomass waste sources to reduce feedstock logistics costs, there are integration requirements including supplying process heat to reactors via cogeneration and efficient product moisture removal by exploiting available excess process heat or steam (Shafie et al., 2018; Hoekman et al., 2017). Transitioning HTC/VTC technologies into industrial-level solid fuel production faces strategic challenges like developing continuous reactors, managing and treating process wastewaters, achieving consistent quality products, engineering durable process equipment, hydrochar dewatering techniques, and replicating performance at a scale that requires extensive ongoing R&D efforts across various disciplines to resolve (Shafie et al., 2018; Hoekman et al., 2017).

2.6 Hydrochar

Hydrochar is a porous carbon-rich material that could be produced through hydrothermal carbonization (HTC) of organic feedstocks. HTC involves heating biomass in water at temperatures typically between 180 – 250 °C under autogenous pressures (Libra et al., 2011). One potential feedstock for hydrochar production is poultry manure, which is produced in large quantities globally. Hydrochar has attracted interest due to its potential benefits when applied to soil, including improving soil fertility, carbon sequestration, and contaminant immobilization (Sun et al., 2014). However, the properties and potentials of hydrochar vary significantly depending on the feedstock and HTC process conditions. Therefore, it is important to investigate further hydrochar specifically derived from poultry manure to understand its unique features, characteristics and applications.

Previous studies have investigated hydrochar production from manure using a range of process conditions. Ghanim et al. (2016) produced hydrochar from chicken manure using temperatures of between 150 °C to 300 °C and residence times of 0.5, 2, 4, and 8 hours. It was observed that the higher heating value (HHV) of hydrochar was related to the changes in C carbon content, and the optimal peak energy was at 250 °C whereas the effect of residence time may be lower. The HHV of poultry liter (PL) was 17.18 MJ/kg and the HHV of hydrochars was in the range of 25.17 – 17.25MJ/kg. In addition, it was noted that the sugar content of hydrochars decreased with increasing treatment temperature and time, with the total sugar contents decreasing from 48.0 to 0.0 %. Overall, the result indicated that the HHV was improved by up to 25.17 % and the overall ash in hydrochar was significantly lower compared to PL.

Moreover, Cao et al. (2021) found that increasing the residence time during hydrothermal carbonization of biogas digestate from cow manure and energy crops slightly reduced the higher heating values of hydrochar but improved its slagging and fouling indices. However, the specific methane yield of the process water was not significantly influenced by the residence time. Song et al., (2018) investigated hydrochars produced from pig manure at different pyrolysis temperatures and residence times. They found that the composition of major elements in the hydrochars varied with reaction temperature and time, with the concentrations of phosphorus, copper, and zinc increasing with higher temperatures and longer residence time. In addition, a study used dried and ground poultry manure, it explored HTC using poultry litter mixed with sawdust. They prepared hydrochar at 220 °C for 1 – 4 hours. Although, this study did not give an account of the moisture of the materials. It was stated that the hydrochar produced has benefits as a soil improver, due to its surface pores and nutrient sorption properties thus increasing water and nutrient retention (Isemin et al., 2021). This method could enable direct HTC processing of raw manure without energy-intensive drying and HTC processing parameters influence the properties of derived hydrochar.

The nature and degree of hydrothermal reactions influence the physicochemical properties of the solid hydrochar produced, including characteristics vital for intended end uses such as process yields, carbon content, energy values, and environmental stability. All comparative studies between HTC and VTC conducted with analogous feedstocks, temperature ranges, and reaction times indicate hydrothermal carbonization proceeds to a greater degree for conventional HTC techniques where feedstock remains submerged in liquid water over the full process timeline (Cao et al., 2013; Shafie et al., 2018; Yeoh et al., 2018). HTC thereby generates hydrochar with higher carbon content and aromaticity along with lower H:C and O:C ratios. These compositional attributes lead to improved heating values. However, enhanced carbonization also imparts heightened environmental stability that reduces biodegradability for the HTC hydrochar products (Ro et al., 2017).

Previous studies have investigated how process conditions like temperature and residence time impact hydrochar properties and energy content. Additionally, work has been done on integrating nutrient recovery into the hydrothermal carbonization process. Heilmann et al. (2014) extracted phosphorus from chicken, swine, and cattle manure through HTC. They produced 50 to 60 % hydrochar yields from the manures at temperatures between 225 and 260 °C. The phosphorus-extracted char had a higher P content (80 – 90 %). This demonstrates how HTC can enable both hydrochar production and phosphorus recovery while tailoring the hydrochar's nutrient profile. The ability to extract and concentrate phosphorus could make this an attractive process for managing manure nutrients.

Furthermore, regarding crop growth, Gondek et al. (2018) showed that amending soil with hydrochar increased the biomass of ryegrass compared to soil with unenriched biochar. Similarly, Manolikaki et al. (2017) found that the addition of biochar significantly increased the dry matter yield of ryegrass. However, a study conducted by (Nelissen et al., 2015) reported that there is a reduction in soil NO_3^- availability, N use efficiency, and biomass yields when compared to a control soil. Research suggests hydrochar benefits crop growth in soils, but effects may vary based on soil properties and hydrochar characteristics. Further field studies are needed across different soils, climates, and cropping systems for deeper insights.

2.7 Activated carbon

Activated carbon is a highly porous material with a large internal surface area, produced when a carbonaceous source materials (hydrochar or biochar) is subjected to activation to increase its porosity (Alabadi et al., 2015; Bansal et al., 1988). Poultry manure represents a potential precursor for activated carbon production due to its high carbon and low inorganic contents. Converting poultry waste into activated carbon can also help manage this abundant byproduct. Activated carbons derived from agricultural residues have shown effectiveness in the adsorption of organic pollutants and gases (Maneerung et al., 2016). Therefore, there is significant interest in utilizing poultry manure as a feedstock for activated carbon.

Different research has investigated the production of activated carbons from various biomass materials, evaluating the effects of different thermal processes and activation conditions. Studies by Lima & Marshall (2005) and Guo (2011) investigated optimal conditions for producing high-quality activated carbon from broiler litter. Lima (2005) determined that steam-activating broiler litter for 45 minutes at a flow rate of 3 ml/min resulted in optimal activated carbon. In contrast, Guo & Song (2011) found that first carbonizing broiler litter at 700 °C for 45 minutes, followed by steam activation at 2.5 ml/min for another 45 minutes, produced activated carbon with superior performance. The differing results highlight the importance of both carbonization temperature and steam flow rate in optimizing the activated carbon production process when using broiler litter as the raw material.

Furthermore, studies have investigated methods to increase the surface area and optimize the properties of activated carbons. Lotz et al. (2019) demonstrated that pyrolyzing raw materials above 300 °C increased carbon content up to 95 wt% and surface area to 520 m^2/g at 600 °C. Lee & Park (2013) found that the chemical activation of activated carbon fibres (ACFs) significantly increased surface area to 2318 m^2/g. Kohli et al. (2015) showed that CO_2 activation of carbon aerogels (CAs) boosted surface area from 698 to 2057 m^2/g. Finally, Rejifu et al. (2009) showed that CO_2 re-activation of pitch-based ACF increased surface area to 2930 m^2/g. The findings indicate pyrolysis, chemical activation, and CO_2 activation can optimize activated carbon properties, especially surface area.

Moreover, activation techniques play a crucial role in enhancing the properties of activated carbons from biomass. Scientific studies have investigated KOH and H_3PO_4 as chemical activating agents for producing activated carbons with high surface area and porosity. Otowa et al. (1996) demonstrated that KOH activation resulted in high-surface-area carbon. Oginni et al. (2019) showed biomass-derived activated carbons activated with KOH had the highest BET surface areas compared to other agents. Comparatively, Villota et al. (2019) found that H_3PO_4 activation of waste cocoa pod husks produced activated carbon with more optimal textural properties versus KOH activation. The research indicates that KOH is effective for achieving maximum surface area, while H_3PO_4 activation may confer superior porosity. The choice of activating agent strongly influences the textural properties of the resulting activated carbon.

Several studies have explored optimized methods for producing high-quality activated carbon from animal waste sources. Huang et al. (2008) developed a three-stage steam activation process using chicken waste to generate activated carbon with comparable mercury adsorption to commercial carbons. Isemin et al. (2021) produced activated carbon via wet torrefaction of chicken manure and sawdust mixtures, followed by potassium hydroxide activation. Manocha et al. (2015) used a polymer blend in a one-step carbonization/activation process to prepare activated carbon from cattle manure compost with enhanced surface area and porosity. Qian et al. (2007) prepared activated carbon from cattle manure compost using zinc chloride activation. The findings demonstrate that activated carbons can be successfully generated from animal wastes through various production methods and have promising adsorption capacities.

In addition, studies have explored the potential of activated carbons from agricultural residues to adsorb and remove phosphorus and ammonia from aqueous solutions. Liang et al. (2011) demonstrated that activated carbon derived from sugarcane bagasse achieved high phosphorus removal percentages ranging from 22.64 % to 99.27 %. Kilpimaa et al. (2015) showed that activated carbon produced from carbon residue obtained after wood gasification effectively adsorbed phosphates. In contrast, Fitzmorris et al. (2007) focused on utilizing activated carbon from broiler litter for ammonia removal. The research indicates that activated carbons from agricultural wastes can serve as promising adsorbents for removing excess nutrients like phosphorus and ammonia from wastewater effluents.

Nonetheless, several studies have investigated agricultural waste-derived activated carbons for removing dyes and phenols from wastewater. Beker et al. (2010) demonstrated excellent adsorption of phenol by cherry stone-based activated carbon compared to commercial carbons and polymers. Liu et al. (2008) found high adsorption capacities of wood waste-activated carbon for methylene blue and phenol, noting the effects of pH, contact time, and initial adsorbate concentration. Abdulkarim et al. (2002) showed date fruit pit-activated carbon had a high uptake of methylene blue and phenols. Mohanty et al. (2005) examined Tectona grandis sawdust-activated carbons, finding substantial phenol adsorption capacity influenced by carbonization conditions and pH. Overall, the research highlights the potential of utilizing activated carbons from agricultural residues as effective and low-cost adsorbents for removing dyes and phenolic pollutants from wastewater.

2.8 Hydroxymethylfurfural (5-HMF)

Hydroxymethylfurfural (5-HMF) is a versatile chemical that can be produced from the dehydration of fructose and other hexose sugars. 5-HMF has attracted significant interest as a building block for the production of biofuels, polymers, and other high-value chemicals (Tong et al., 2010). It is considered one of the top value-added chemicals derived from biomass by the U.S. Department of Energy (Tiwari et al., 2022; Shao et al., 2021). 5-HMF can be produced from various biomass sources, including agricultural residues, energy crops, and waste materials. One particularly promising feedstock is poultry manure, which contains substantial amounts of carbohydrates that can be converted to 5-HMF (Isemin et al., 2021).

Poultry manure is generated in large quantities as a byproduct of the poultry industry. It is estimated that over 1.4 billion tons of poultry waste is generated annually in the United States alone (Courtney, 2019). Typical components of poultry manure include undigested feed, bedding materials, feathers, faecal matter and urine. Carbohydrates make up 25-50% of poultry manure on a dry-weight basis, primarily in the form of cellulose and hemicellulose (Nahm, 2003; Nicholson et al., 1996). These polysaccharides can be broken down into monomeric sugars and further dehydrated into 5-HMF. Utilizing poultry waste as a feedstock for value-added chemicals like 5-HMF can improve the sustainability and economics of poultry production.

Most studies on 5-HMF production from biomass utilize some form of pretreatment to make the carbohydrates more accessible for dehydration reactions. Chen et al. (2017) examined the effects of different pretreatments, including acid, alkaline, ionic liquid, and hydrothermal methods. The pretreatment of woody biomass species, such as pine, spruce, eucalyptus, and mixed southern hardwood, has been studied at 150 – 240 °C for 1 – 118 minutes using sulfuric, acetic, oxalic, formic, and maleic acids (Larsson et al., 1999; Gütsch et al., 2012; Tunc et al., 2014). There is a linear correlation between the amount of hardwood that dissolved and the concentration of acetic acid after treating the hardwood with acetic and formic acid for 90 minutes at 160 °C (Tunc et al., 2014). In contrast, Pu et al. (2013) accomplished 24% softwood solid dissolving following autohydrolysis at 180 °C for 120 minutes. Lim and Lee (2013) were able to dissolve 20 – 25 % solids from softwood by employing acid at 160 – 180 °C for 30 – 118 minutes. Acid pretreatment removes hemicellulose and lignin, exposing the cellulose for subsequent enzymatic conversion to sugars.

Lim and Lee (2013) examined how sulfuric, oxalic, and maleic acids affected the hydrolysis of mixed softwood. According to their study, sulfuric acid accelerated the hydrolysis of softwood more quickly than other acids. Sulfuric acid is commonly used, but other acids like maleic acid, phosphoric acid and nitric acid have also been studied (Paulraj et al., 2022; Mussatto, 2016; Idrees et al., 2013). Sulfuric acid pretreatment can achieve relatively high yields (Singkhornart et al., 2013), but requires special corrosion-resistant reactors and has to contend with recycling large volumes of acidic wastewater. Alternative pretreatments have been explored to overcome some of the downsides of acid hydrolysis. Alkaline pretreatment (Kim et al., 2016), extrusion pretreatment (Zheng & Rehmann, 2014), and dilute acid hydrolysis (Chandel et al., 2012), have been explored to overcome some of the downsides of acid hydrolysis in the bioconversion of lignocellulosic biomass. These pretreatment methods aim to enhance hydrolysis by removing or altering structural and compositional impediments of the biomass. Alkaline pretreatment selectively removes lignin without degrading carbohydrates, while partial acid hydrolysis removes hemicellulose and reduces the degree of polymerization of cellulose (Wang et al., 2015). Extrusion pretreatment using twin-screw extruders has also been investigated, and dilute acid hydrolysis has shown promise in breaking down hemicellulosic fractions into sugars (Singkhornart et al., 2013; Chandel et al., 2012).

Deep eutectic solvents (DES) are a relatively new class of ionic solvents that have shown promise as both catalysts and solvents for 5-HMF synthesis (Liu et al., 2015). These solvents are formed by mixing a hydrogen bond donor (like choline chloride) with a hydrogen bond acceptor (like urea) (Santha Kumar & Singha, 2019). Yao et al. (2022) found that a combination of DES and ethanol pretreatment resulted in enhanced glucose yield and delignification in various biomass samples. Wang et al. (2020) demonstrated that a novel DES coordinated with $FeCl_3$ showed excellent pretreatment performance, retaining most of the cellulose and significantly increasing cellulose saccharification. Moreover, Hou et al. (2017) showed that a two-stage DES treatment with a specific order and the presence of water improved sugar yield and cellulose recovery.

A recent review carried out by Wang & Lee (2021) about the application of DES in biomass pretreatment, highlighted its potential for lignin extraction and saccharification enhancement. The high viscosity resulting from the strong hydrogen bond of some DES can impede mass transfer. However, DES appear to be a green alternative to mineral acids, but more optimization is needed to improve 5-HMF yields. Furthermore, alternative dehydration methods without acids have also been studied. A promising catalyst-free option is subcritical water, which uses hot compressed water at temperatures of 100-374°C (Jeong et al., 2017; Lachos-Perez et al., 2017; Möller et al., 2011). Subcritical water provides sufficient heat for dehydration while maintaining a lower temperature than supercritical to avoid unwanted decomposition reactions. Further process intensification could make this a viable approach for streamlined 5-HMF production directly from wet poultry waste.

2.8.1 Purification and yield optimization

A persistent challenge with 5-HMF production is the purification of the product from complex reaction mixtures. The main byproducts are formic acid from sugar decomposition and levulinic acid from 5-HMF rehydration (Mukherjee et al., 2015). Solid acid catalysts like Amberlyst resins have demonstrated excellent selectivity to 5-HMF over acids, potentially simplifying purification (Binh et al., 2016). Deep eutectic solvents also remain liquid during the reaction, allowing selective extraction of 5-HMF into an organic overlaying solvent (Karimi et al., 2020; Pena-Pereira & Namieśnik, 2014).

Various organic solvents, adsorbents, and other techniques have been tested for isolating 5-HMF from aqueous reaction mixtures. Sayed et al. (2020) and Sindermann et al. (2016) discovered that 5-HMF can potentially be effectively isolated using methyl isobutyl ketone (MIBK), especially when used in a countercurrent extraction procedure. Similarly, Sonsiam et al. (2019) used a biphasic system using MIBK as the organic solvent to generate large yields of 5-HMF. The selective adsorption of 5-HMF from aqueous solutions onto nano-porous hyper-cross-linked polymers was reported by Detoni et al. (2014). In another study conducted based on a predicted thermodynamic model, Blumenthal et al. (2016) established that o-propylphenol and o-isopropylphenol were suitable solvents for 5-HMF extraction.

Nanofiltration membranes are also promising for separating 5-HMF from acids and unreacted sugars (Sarwono et al., 2019; Saha & Abu-Omar et al., 2014). Integrated reaction-separation systems that continuously extract 5-HMF during production could achieve excellent yields and purity. For instance, Shamsul et al. (2018) designed a co-hydrothermal reaction and extraction that gave a 5-HMF yield of about 39 % alongside 22.97 % carboxylic acids, 0.97 % of aromatic and 0.73 % aldehyde compounds. In a similar manner, more sophisticated and integrated systems must be developed for selective 5-HMF purification from complex poultry manure.

Aside from separation challenges, the maximum 5-HMF yield is limited to 61 % under optimized conditions using ionic liquids, the yields might have been limited due to competing rehydration and polymerization reactions (Wang et al., 2021). To overcome these limitations, some studies have reacted 5-HMF further to form downstream products. One important step in buffering the molecule from degradation is the oxidation of 5-HMF into 2,5-furan-dicarboxylic acid (FDCA) (Han et al., 2016, Rass et al., 2015; Siankevich et al., 2014; Rass et al., 2013). In addition, hydrogenating 5-HMF into 2,5-dimethylfuran (DMF) also gives a more stable liquid product (Pisal, & Yadav, 2021). An array of catalysts can be used to accomplish this reaction, such as Pt catalysts supported on TiO_2 and ZrO_2 (Rass et al., 2015), Pt nanoparticles stabilized by PVP (Siankevich et al., 2014), and Pt/C–O–Mg catalyst (Han et al., 2016). The stability and total catalytic activity of the catalysts may be greatly increased through the addition of a base, like Na_2CO_3 (Rass et al., 2015; Rass et al., 2013). Integrated processes that react 5-HMF into derivatives like FDCA or DMF could therefore achieve higher overall yields from poultry litter carbohydrates.

2.9 Literature Gap

One major gap in the literature is a lack of studies directly comparing hydrothermal carbonization (HTC) and vapourthermal carbonization (VTC) using the same reactor systems and feedstocks. Most previous studies have focused on either HTC or VTC independently, often using different process conditions and biomass materials. Directly analogous studies enabling controlled comparison of variables like heating methods, condensate handling, feedstock interaction kinetics, and resulting hydrochar properties are limited. More parallel HTC and VTC experiments controlling reactor configurations could provide clarification on the advantages, disadvantages and tradeoffs between the techniques.

Additionally, few analyses have probed hydrothermal reaction kinetics and mechanisms specific to manure feedstocks. Most HTC/VTC works have centered on lignocellulosic biomass or municipal wastewater sludges. Whereas manures have compositional differences in carbohydrates, proteins, lipids and nutrients that could substantively influence hydrothermal carbonization pathways based on existing outlines of the process chemistry. Manure-based HTC/VTC especially poultry liters' likely warrants dedicated kinetic models and an understanding of how inorganic components impact intermediate formation and hydrochar restructuring.

Furthermore, the majority of HTC/VTC hydrochar analyses have focused on fuel properties. However, research gaps remain regarding optimal post-processing steps for hydrochar end uses. Most studies report an air-dry simple filtered hydrochars without further activation or procedures tailored to different applications. Investigating the treatment effects of various conditioning methods on hydrochar functionalities could reveal preferred pathways for enhanced value addition.

Additionally, few works have explored integrating heat recovery or cogeneration concepts to improve HTC/VTC sustainability. The exothermic nature offers thermal integration opportunities to reduce reliance on external heating energy demands. However, harnessing excess heat or steam from intermediates would require overcoming engineering and safety challenges for novel self-sustaining systems. Process modelling incorporating physical activation by steam highlights largely unexplored possibilities for increasing HTC/VTC viability through thermal efficiency gains.

Furthermore, research gaps persist regarding the sustainable handling of process waters from these processes. HTC to be particular generate large volumes of process water containing high organic carbon content and simply discharging these process waters is not an environmentally friendly disposal route because of their great potential to cause a greenhouse effect. Most studies have air-dried small hydrochar batches instead of testing more scalable processes and water management approaches. Evaluating emerging wastewater treatment technologies like bioremediation method especially using algae could uncover preferable alternatives to manage these high-strength process waters and their carbon loads sustainably. Further research would assess potential technologies from a life cycle perspective especially on algae growth to identify optimal solutions for mitigating the environmental impacts of process waters from these hydrothermal conversions.

Additionally, other process like gasification for waste treatment as focused on syngas production without exploring char production. Evaluating and focusing on direct conversion of the biowaste would be explored using a syngas approach called steam at high temperature or direct steam activation to tailor the production of activation char instead of the reported syngas.

Furthermore, the research gap identified lies in the limited exploration of blending pyrolysis with inert gases and subsequent activation. While some studies have delved into only pyrolysis, this research explored the existing body of knowledge by specifically focusing on the utilization of inert gases in the production of activated char. Evaluating the need for a more comprehensive understanding of the potential benefits and outcomes of incorporating inert gases into the pyrolysis process for char activation was explored in this report.

While few analyses have systematically optimized activated carbon production from HTC rather than solely assessing and comparing other methodological approach, this studies report the design of activated chars using conventional methods with the goal of necessarily maximizing properties like surface area or porosity based on the specific precursors. Comparing activation agents, thermal patterns, and post-treatments tailored to activated char formation could improve quality where direct competition with commercial carbons exists.

This research also explored the production of 5-HMF, activated char and application of activated char in water treatment and energy storage application.

2.10 References

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CHAPTER THREE

3.0 GENERAL METHODOLOGIES

3.1 Materials and Feedstocks Preparation

Poultry litters consisting of chicken manure and sawdust were used for this study. The chicken manure (M) was collected from a poultry industry while the sawdust (S) was produced from pine wood and collected from a wood processing factory in Russia were mixed in percentage proportionality of 1:0 (S), 2:1 (S67M33), 1:1 (S50M50), 1:2 (S33M67), 0:1(M), as shown in Figure 3a-e respectively and transported to the Institute of Chemistry, Carl von Ossietzky Universität of Oldenburg. The substrates which total 5 were received dry and in fine particles of about 0.01 µm in sizes is shown in Figure 3.0.

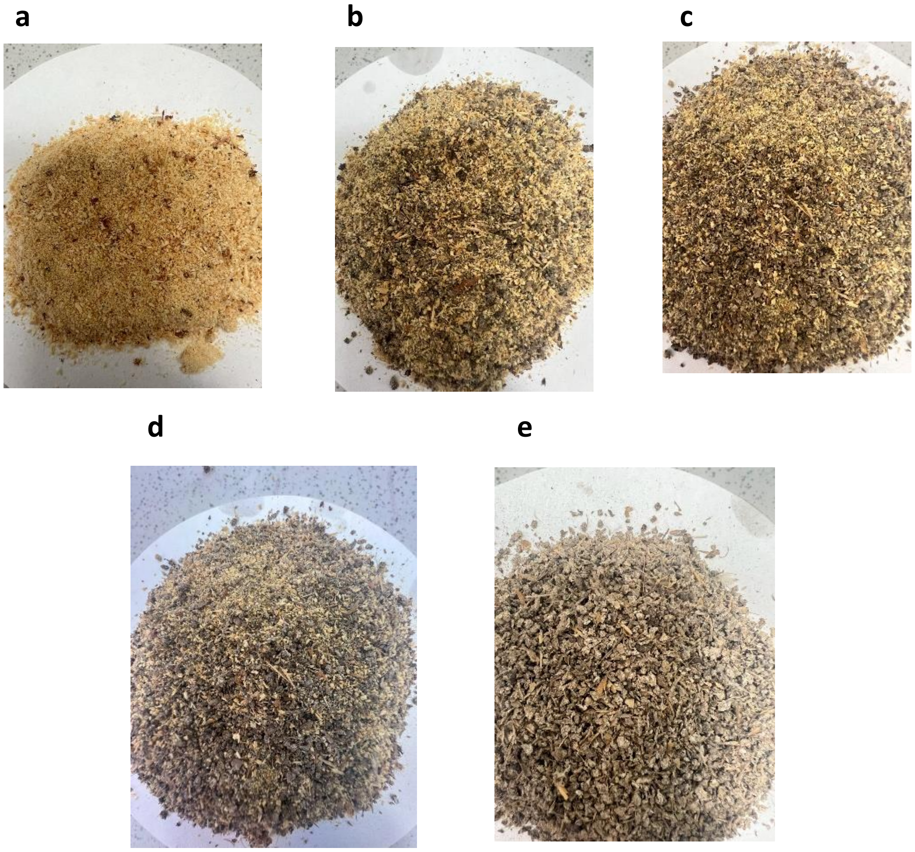

Figure 3a-e: *Poultry litters (PL) mixed in varied proportion*

3.2 Experimental Methods

3.2.1 Standard HTC

A comprehensive methodology for Hydrothermal Carbonization (HTC) experiments, with a focus on exploring the influence of reaction temperatures and carbonization time is presented in this report. This study was conducted in an unstirred 500 mL, high-pressure oven reactor, which allowed for controlled systematic investigation. The samples were loaded in an autoclave (Figure 5b) before been put into the oven(Figure 5c). In each experiment, the autoclave liners (Figure 5a) was loaded with 10 g of substrates and 90 g of distilled water. To analyze the effect of the operating conditions on the feedstock's, the experiment was performed at different reaction temperatures of 200 and 220 °C at a residence time of 2 and 4 hours. The overall temperature and time profile of the experiment was made constant for each reaction conditions. The pressure was kept autogenic with the vapour pressure of water. Soon as the residence time was reached, the reactor was brought out and put into the fume hood to cool down to room temperature before been separated using filter paper. The separation which consists of the process water and the solid residue also known as the char was separated using a filter paper of size 20 µm. The solid residue after been separated was stored in the oven for 3 days at 80°C for drying while the process water obtained from each experiment was further analyzed.

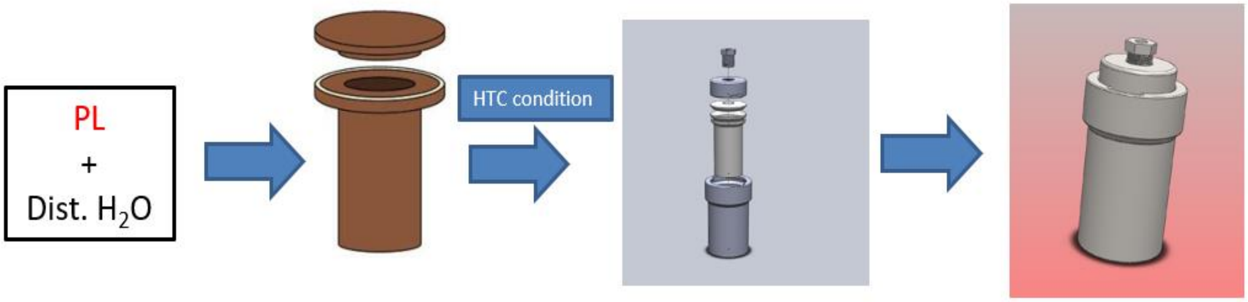

Figure 4: *Experimental pathway for Hydrothermal Carbonization of Poultry litters*

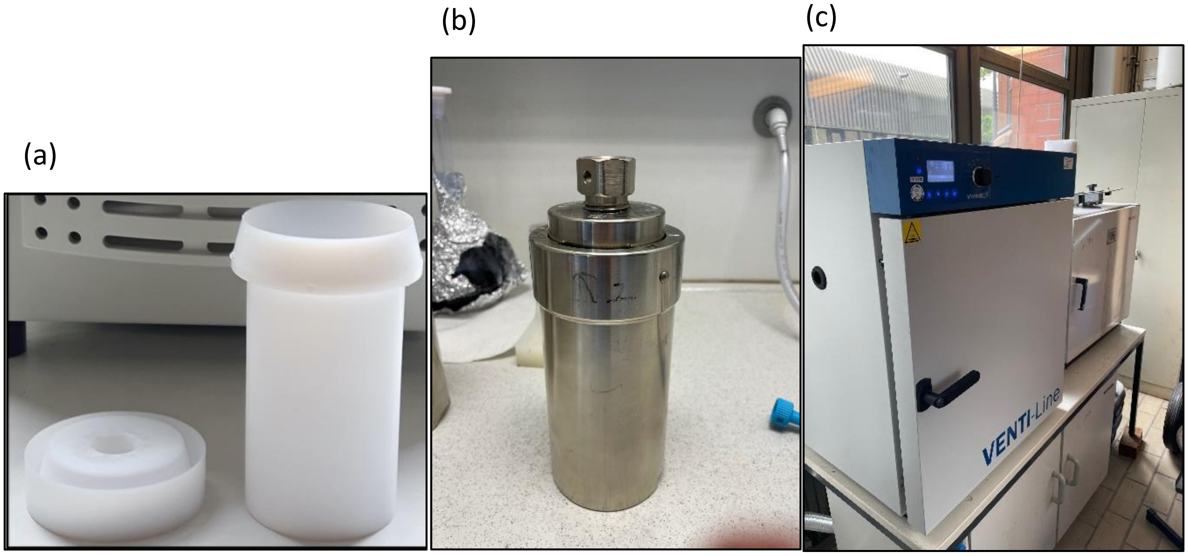

Figure 5: *Experimental Carbonization Utensils consisting of (a) liners (b) Autoclave (c) Microwave oven*

3.2.2 Two–step HTC

The modified two-step HTC method requires the hydrothermal pretreatment (hydrolysis) of substrates and replacement of the process water with fresh distilled water after pretreatment and heating up to the required carbonization temperature (Figure 6). The substrates were first hydrolyzed at different temperatures of 130, 150 and 170 °C at a residence time of 1 and 3 hours which is termed short and long hydrolysis conditions in regards to the residence time in this study. Soon as the hydrolysis time was reached, the samples were separated and the char obtained from hydrolysis was further prepared for carbonization. Hydrothermal pretreatment (hydrolysis) and carbonization of each substrate was performed at a ratio of 1 to 10 w/w of biomass to distilled water. As soon as the carbonization residence time was reached, the autoclave was brought out and placed into the fume hoods for cooling before been separated using filter paper. To evaluate the accuracy of both hydrothermal methods, the reaction conditions such as time was kept constant for both the usual standard HTC and modified two-step HTC methods at 4 hours. The sole aim of the two-step HTC was to optimize the amount of 5-HMF produced and therefore, only its process-water analyses is reported in this study.

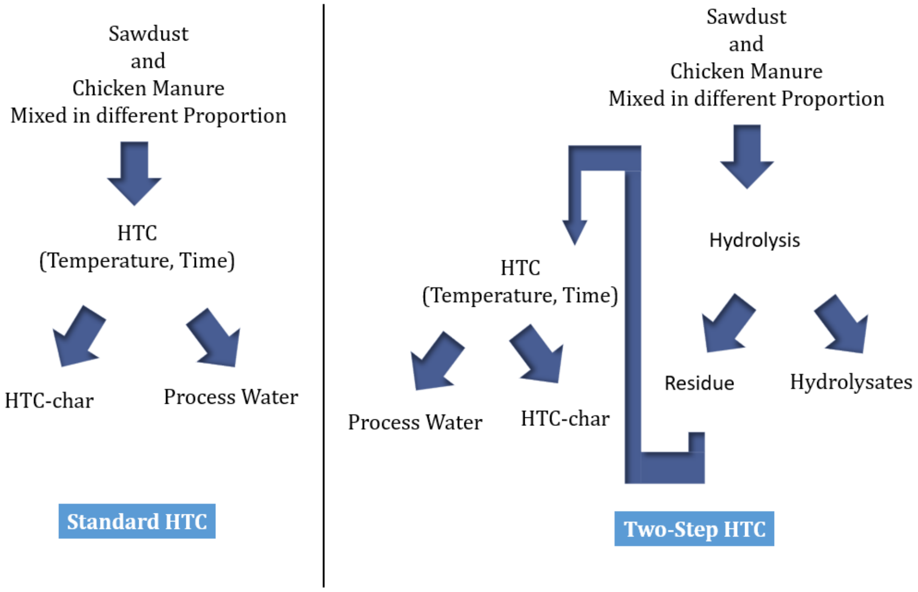

Figure 6: *Reaction Pathways for Standard HTC and Two-step HTC*

3.2.3 Direct steam activation

A comprehensive methodology for the direct steam activation of poultry litter for the production of activated carbon was explored in this research. This method involves the direct activation of the poultry litters using steam at elevated temperatures (ST) without a prior carbonization method, resulting in the production of activated carbon. In this process, the starting material (sawdust and chicken manure) is subjected to steam at elevated temperature under controlled conditions, which leads to the removal of volatile components and the development of a porous structure within the material. For synthesis, the feedstock's was placed directly in the crucible without any prior pretreatment and then carbonated using steam at a temperature between 650 – 800 °C with N_2 gas supplied into the activation oven to aid the steam to the surface of the feedstock. The synthesis of the sample occur in an activation oven shown in figure 7.

Figure 7: *Steam activation oven for ST treatment of PL*

3.2.4 Pyrolytic pretreatment

This research delve into the intricate methodology used for Pyrolytic Pretreatment (PYC) as a novel approach to produce activated carbon, demonstrating it's potential to rival or even surpass the quality of activated carbon produced through conventional direct steam activation (ST). This method incorporates the introduction of inert gases such as N_2 and CO_2 while also considering a no gas (NG) during Pyrolytic Pretreatment, followed by the selection of carbon produced via this pretreatment process, and its subsequent activation. While this method is similar to the direct steam activation, this method investigated the pyrolytic pretreatment of the starting material prior to the direct steam activation. The primary goal of this method is to reduce the low yield associated with the direct steam activation while also producing an intermediates char which was further treated using steam activation for the production of activated carbon. The pyrolytic temperature used during this method was 750°C at a residence time of 0.5 and 1 hour. After pretreatment, carbon with high yield was selected for further steam activation at 750°C for 1 hour and further characterization was carried out.

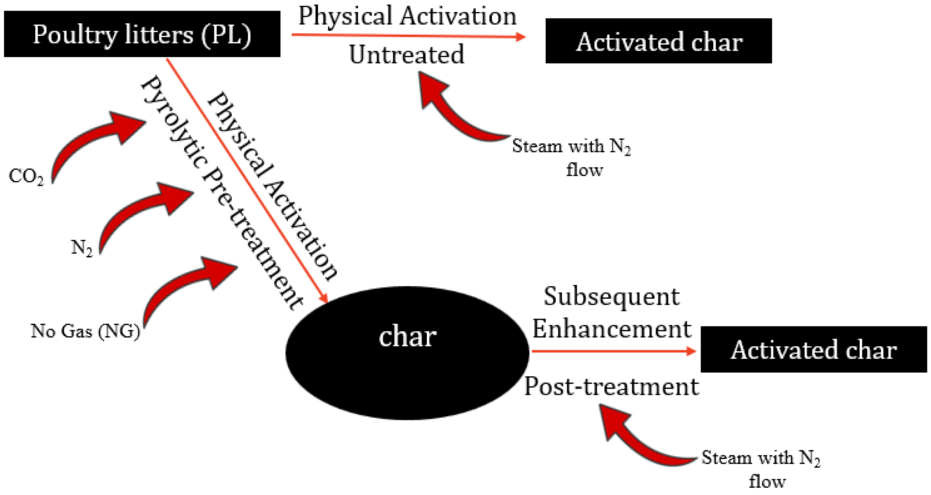

Figure 8: *Reaction pathway for ST and PYC Treatment*

3.2.5 Vapourthermal carbonization

The methodological approach for vapourthermal carbonization (VTC) is a process that distinguishes itself from hydrothermal carbonization (HTC) by its exclusive utilization of vapour and without direct contact between water and feedstock. Additionally, this method was adopted in this research to cater for large amount of process water obtained in the usual HTC and two-step HTC. To achieve this, a novel VTC reactor design with specially engineered vapourthermal basket that ensures separation between the feedstock and water was design (Figure 9). This separation is critical as VTC hinges on the interaction of vapour solely with the feedstock, setting it apart from HTC where water plays a more prominent role in the reaction process.

Figure 9: *Vapourthermal basket/inlet*

Before embarking on the VTC process, it is imperative to assemble the requisite materials and equipment for seamless execution. The methodology for this process is quite the same as the HTC with similar carbonization temperature and time. The feedstock was loaded in the vapourthermal basket/inlet and then loaded to the autoclave which already had distilled water in it. Carbonization was then carried out at temperature of 200 and 220 °C for 2, 4 and 6 hours. After carbonization, the char from the VTC basket was collected and dried in the oven at 80 °C for 3 days while the distilled water enabling the vapour now process water was collected and save for further analysis. The setup arrangement for the VTC experimental setup is shown in Figure 10.

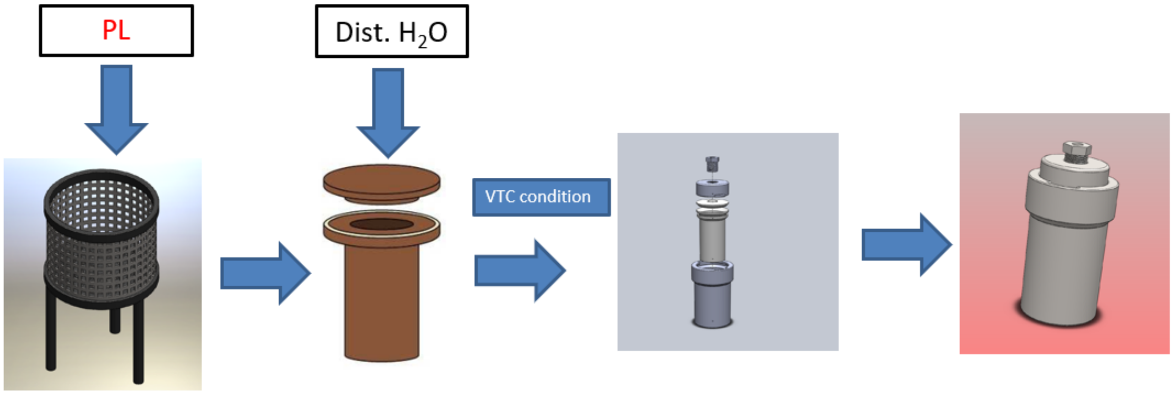

Figure 10: *Reaction Pathway for Vapourthermal Carbonization*

3.3 Physical or steam activation

Steam activation or physical activation by steam is an essential method in the production of activated char. Steam activation is a thermochemical process that transforms carbonaceous materials (chars) into a highly porous and adsorbent activated carbon. The chars produced via HTC and VTC were further activated at higher temperature of 650 °C at a reaction time of one hour to produce activated char while others produced via direct steam activation and pyrolytic pretreatment needs no further activation. Before the activation process, a measured quantity of the char was carefully placed in a small ceramic crucible and weighed using a precise balance. The activation furnace was then set to the required target temperature, and heat wool insulation was priorly applied to minimize heat loss as shown in Figure 7. Once the activation furnace has reached the stable and targeted temperature, an oil bath was prepared and heated to approximately 130°C. This is to help boil the water dipped into the oil at a particular depth. The water beneath the oil bath was then stirred at 350 rpm to help move the steam to the top of the hydrochar. As soon as the oil bath reached the desired temperature, the hydrochar-filled ceramic crucible was swiftly and cautiously placed into the heat chamber, using heat-resistant gloves and a suitable tool, and the gas supply was activated. Speed was of the essence to minimize heat dissipation. The nitrogen gas supply was then opened, initiating the activation process, which was allowed to continue for a duration of one hour. After one hour, the furnace temperature was gradually reduced to approximately 75 °C and the insulation material was carefully removed using suitable tools, and the gas supply was turned off during the cooling. The crucible, now containing the activated char, was cautiously removed and placed in the fume-hoods. The resulting activated char was weighed before been transferred to a properly labeled sample holder. To ensure uniformity and prevent clumps that might interfere with subsequent analysis, the activated char was gently crushed using a metal spatula prior to storage and was stored for analysis.

Figure 11: *Activated Char*

3.4 Analysis Method

To compare several methodological approach employed in this research report, analysis such as process water analysis and characterization of activated carbon was carried out.

3.4.1 Process water analysis

The process water produced as a by-product of carbonization during HTC and Two-step HTC presents a valuable opportunity for the recovery of sustainable raw materials. Three critical parameters were investigated in this context: pH value, the concentration of 5-Hydroxymethylfurfural (5-HMF) and the total organic carbon (TOC) present in the process water was reported in the study.

3.4.1.1 pH measurement

The pH value serves as a fundamental indicator of the hydrogen ion concentration within an aqueous solution, defining its acidity or alkalinity. This research employed a pH meter based on potentiometry, a technique that measures the voltage between a reference electrode and an indicator electrode. This voltage differential varies depending on the pH difference between the solution being measured and a buffer solution. The pH value of the process water was measured using a pH meter, and the results were collected and presented in this report.

Figure 12: *pH Meter*

3.4.1.2 5-Hydroxymethylfurfural (5-HMF) concentration

5-HMF, an abbreviation for 5-Hydroxymethylfurfural, is a significant value-added chemical compound that is generated during the dehydration of fructose and has versatile applications. This unique property renders it valuable in pharmaceuticals, polymer industry, and production of diverse solvents. To measure the 5-HMF concentration present in the process water, a reflectometer was used which employs the principles of reflectance photometry. This technique entails the measurement of light reflected from a test strip. Similar to photometry, the difference in intensity between emitted and reflected light facilitates the determination of 5-HMF concentrations. A 5-HMF test strips were dipped into the process water and set aside before it is been inserted into the reflectometer. 5-HMF is measured in about 120 seconds and in roughly 32 seconds left, the test strips is inserted into the reflectometer. If the concentration exceeded the measurement range, the process water was appropriately diluted. Following this preparation, the test strip was inserted into the reflectometer as shown in Figure 13, and the instructions displayed on the screen were diligently followed. After approximately 120 seconds, the results were displayed which provided the insight into the 5-HMF concentration present in the process water.

***Figure 13**: 5-HMF measurement using a Reflectometer*

3.4.1.3 Total Organic Carbon (TOC)

TOC is a critical parameter that quantifies the total concentration of organic carbon compounds present in the process water. It is a valuable indicator of the overall organic content and can help assess the degree of contamination or the presence of organic pollutants in water. The measurement of TOC was carried out using a specialized TOC analyzer by Shimadzu's TOC-V CPH. This analytical instrument is designed to oxidize all organic carbon compounds present in the sample to carbon dioxide (CO_2), which is subsequently quantified using various detection techniques such as non-dispersive infrared (NDIR) spectroscopy. This precise analytical technique enables the quantification of TOC with remarkable accuracy, offering crucial insights into the organic composition of the process water. For the analysis, each process water sample was introduced into the TOC analyzer after it has been diluted as per standards. The instrument subjected the sample to high-temperature combustion or chemical oxidation to convert all organic carbon species into CO_2. The generated CO_2 was then quantified, and the TOC concentration was determined. The results provide valuable insights into the overall organic content in the process water, which is essential for assessing the quality and environmental impact of the water produced during the carbonization process. The TOC analyzer is presented in (Figure 14) is connected to a computer with specialized software, and help to facilitate these analyses and display each TOC results contained in the process water. The results were noted and is presented in this report.

Figure 14*: TOC analyzer by Shimadzu's TOC-V CPH*

3.4.2 Char morphology analysis

Analyzing the morphology of the char (activated char and char produced from various carbonization method) is essential for understanding its properties and suitability for various applications and to differentiate carbonization method. Several analytical methods were employed to assess the characteristics of the activated char produced via HTC, ST, PYC and VTC. The detailed analysis methods used for the characterization of the hydrochar and activated char is highlighted in this subchapter.

3.4.2.1 Elemental analysis (EA)

Elemental analysis, often referred to as CHN/S analysis, stands as a cornerstone in the systematic evaluation of the activated char, unraveling its elemental composition down to the most intricate details. This data, encompassing the proportions of carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O), plays a pivotal role in discerning the char's chemical constitution and, notably, its expansive potential across various applications. For the determination of the elemental composition of the activated char, a EuroEA Elemental Analyser (HEKAtech GmbH) was used. The analysis begins with the introduction of the char sample into an analytical furnace via an autosampler. This is where the the sample is primed for an orchestrated transformation. Inside the furnace, the sample undergoes complete oxidation, meticulously orchestrated in the presence of oxygen. The temperature ascends to a scorching 1020 °C, a crucible of intense heat where the essence of the char is unraveled. Following combustion, the resulting gases traverse a path where they encounter copper granules, guided by a carrier gas (typically helium). This strategic encounter serves a dual purpose: it quenches the possible formation of nitrogen oxides while leading to the conversion of such compounds into molecular nitrogen. The journey doesn't conclude here. The amalgamation of gases, now meticulously purified, ventures into the next phase. Here, a gas chromatographic column acts as a discerning filter, paving the way for individual elements to express their unique signatures. As the gases course through the column, their presence is unveiled and monitored by a thermal conductivity detector (TCD). This meticulous detector is attuned to nuances in thermal conductivity, skillfully discerning the differential between the sample gas and a reference gas. The elemental analyzer, the sage conductor of this analytical orchestra, harmoniously integrates the information from the TCD. At its crescendo, the analyzer imparts the elemental percentages, thoughtfully demarcating the char's elemental composition based on its original weight. The amount of oxygen was estimated as the difference between 100 % and the cumulative percentages of the other elemental constituents as shown in equation[1]

$$O\% = 100 - C(\%) - H(\%) - N(\%) - Ash(\%) \qquad [1]$$

3.4.2.2 Ash Content

The ash content analysis is a pivotal method used to quantify the inorganic mineral residue present within activated char. Understanding of the ash content is vital for various applications, as it impacts the char's purity and suitability for specific uses. The ash present in each activated carbon was estimated in a precisely controlled, high-temperature incineration process using the ASTM D3174-02 method for coals. The amount of ash was determined by determing the weigh residue remaining after burning the sample under a controlled conditions. During this stage, the organic carbon components of the activated char are oxidized, leaving behind the inorganic mineral content in the form of ash. The resultant residue, commonly referred to as ash, was then accurately quantified. This quantification was achieved by measuring the weight differential before and after incineration and was expressed as a percentage of the initial sample weight. To achieve this,a weighed crucible containing the sample was loaded into a cold furnace and heated gradually such that a temperature of 500 °C was achieved in 1 hour before a second stage of heating was continued to achieving a final temperature of 750 °C in another 1 hour. The final temperature of 750 °C was then held at constant for a additional 2 hours before it been cooled down to room temperature and the ash content was calculated using equation[2].

$$Ash\ content = \frac{m}{m_0} \times 100\ [\%] \qquad [2]$$

3.4.2.3 X-ray diffraction (XRD)

XRD analysis is a powerful technique that unveils the crystalline structure, phase composition, and lattice parameters of the carbon materials (char). It plays a vital role in characterizing the structural properties of substances, making it invaluable for a wide range of applications, from material science to geology. The hydrochar material is carefully prepared for analysis. The sample was pulverized into a fine powder to ensure a uniform, flat surface and carefully placed in the XRD sample holder and placed into the XRD instrument. An X-ray beam was directed onto the sample and the X-ray photons interact with the electron cloud of the sample's atoms, leading to diffraction patterns. The diffracted X-rays are captured on a detector, resulting in a diffraction pattern. This pattern comprises peaks and troughs, with each peak corresponding to a specific crystal plane or lattice spacing. The diffraction pattern was then collected and analyzed to determine the positions and intensities of the peaks. These characteristics were then used to identify the crystal structure and phase composition of the material. Also, the peak structure of the char produced during two-step HTC and several HTC were compared to the cellulose to have a clearer view of the cellulosic degradation during treatment for the production of 5-HMF. The XRD equipment used for this experiment is shown in Fgure 15.

Figure 15: *XRD Equipment*

3.4.2.4 Nitrogen soprtion or Brunauer-Emmett-Teller (BET) analysis

Nitrogen sorption or BET analysis is a versatile technique that was used to investigate the porosity, specific surface area (SSA), and adsorption properties of the activated carbon material. This method is instrumental in understanding the structural and textural features of porous carbon. In nitrogen sorption analysis, nitrogen gas was introduced into the activated chars, under elevated pressure. This method allows a comprehensive examination of the material's porous properties. During this process, a portion of the gas is adsorbed onto the material's surface and subsequently desorbed. This method not only enables the determination of the surface area but also offers insights into the nature of pores within the 2 to 20 nanometer range classified into three main categories: macropores (greater than 50 nm), mesopores (ranging from 2 to 50 nm), and micropores (defined as less than 2 nm):

To measure the specific surface area (SSA) or pore volume (PV) and determine the proportion of meso- and micro-pores, the samples must undergo a meticulous preparation process. They are first heated and evacuated after being weighed in the degassing station (Figure 16b). This step serves to remove any compounds, such as residual moisture, which might be adsorbed on the surface of the activated char. The samples were then attached to the measurement device and placed in liquid nitrogen at 75 K using a Dewar (Figure 16a) to ensure a consistent temperature for the analysis. The analysis was conducted using an analyzer from Micromeritics, complemented by a vacuum degasser from the same company (Figure 16c). Following the analysis, sorption isotherms are generated on the computer, providing valuable information about the morphology.

Particular interest are the hysteresis curves, which shed light on the adsorption and desorption patterns of the activated carbons. Hysteresis that results in an increase in adsorption and desorption against relative pressure, thus resulting in distinct isotherms. This isotherms are termed meso-pores while those without an increase against relative pressure is termed micropores. While it is possible to measure the meso and micro pores using the sorption analysis, it is quite impossible to see the macropores.

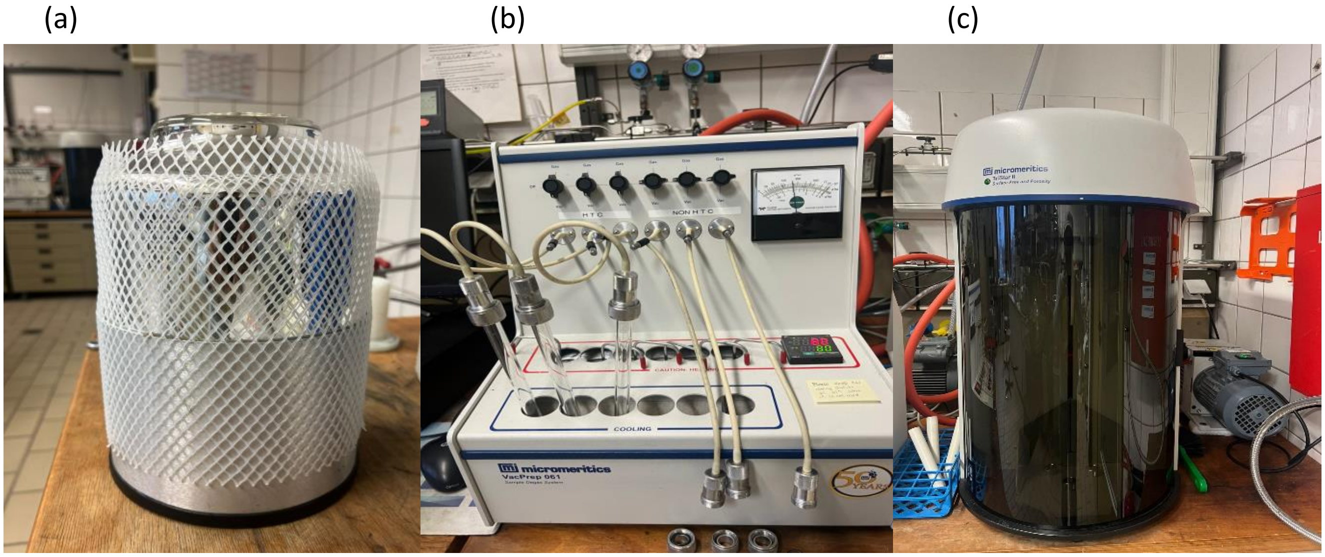

Figure 16a-c: *Dewar (a), Degassing station (b) and Micromeritics analyzer (c)*

3.4.2.5 Mercury intrusion porosimetry

The mercury intrusion porosimetry was used to determine the pore sizes of activated char containing larger pores such as macropores. This analysis is a valuable tool that helps to understand the pore structure of a wide range materials thereby providing the knowledge of the porous material. In this research, the mercury intrusion porosimetry was used to measure the pore sizes of activated char containing possibly larger pores such as macropores. The mechanism relies on a principle of capillary intrusion. The instrument consists of a high-pressure chamber, a sample holder, and a mercury source shown in Figure 17. The activated char was placed in the sample holder, and mercury was injected into the sample at increasing pressures. The intrusion of mercury into the pores was then monitored by measuring the change in the volume of mercury in the high-pressure chamber. The intrusion pressure data obtained during the test was used to generate a pore size distribution curve after the instrument had measured the volume of mercury intruded at various pressure and the information is converted into pore size data.

***Figure 17**: Mercury Intrusion Porosimetry*

3.4.2.6 Scanning electron microscopy (SEM)

The surface morphology of the activated char was taken to have an understanding of the pores on the surface of activated carbon. SEM images of char and activated carbon produced from HTC, VTC, ST and PYC was taken and compared to have a better insight on their thermal degradation and pore structures.

3.4.2.7 Fourier Infrared spectrometry (FTIR) analysis

The Attenuated total reflectance (ATR) fourier transform infrared (FTIR) spectroscopy of the activated char was analyzed and compared with the raw samples in this research. For this analysis, a Bruker Tensor 27 ATR-FTIR spectrometer was used to analyze the chemical structure of the feedstock and the hydrochars. Spectra were collected over 50 scans, at a resolution of 2 cm^{-1}, and over a range of 400–4000 cm^{-1}. Each collected spectrum was measured in ambient air against that of ambient air as a background spectrum. Data was processed using the software OPUS 6.5 carrying out atmospheric correction for carbon dioxide and water. The result is presented of this analysis is reported in this report.

3.5 Application of activated Char

3.5.1 Carbon electrode for Energy storage

Applications of selected activated char was studied and reported in this report. Application such as carbon electrode for energy storage in Na-ion batteries and for water treatment as methylene blue dye absorption. This study gives an overall important of the activated char.

3.5.1.1 Preparation of active material

The active material was prepared using 0.91 g of V_2O_5 and 0.93 g of $C_{17}H_{22}N_2O$ dissolved in a mixture of 5 mL of C_2H_5OH and stirred for 1 hour. 15 mL of de-ionized H_2O were then introduced into the solution and were furtherly stirred using a magnetic bar for 72 hours. After a homogenous and aged mixture was obtained, the solution was put into a glass autoclave and heated at 180 °C with a maximum pressure of 20 bar for 8 hours using a discover CEM microwave. The final products were washed with ethanol to get rid of the residue and centrifuged at 4500 rpm for 15 minutes. The obtained solution was decanted, and the obtained powder was heated in a convection oven at 80 °C for 24 hours at a pressure of 50 mbar.

3.5.1.2 Electrode preparation and cell development

Electrodes were prepared from a slurry consisting of 70 w% of active material, 20 w% of the activated carbon and, and 10 w% of polyvinylidene fluoride (PVDF) used as the binder in a solvent of ethylene glycol. For homogenous mixture, the slurry was allowed to mix for 24 hours before been coated over an oxide free aluminium foil for current collector and then dried at 80 °C for

24 hours. Electrodes of 12 mm diameter were cut from the aluminium foil and prepared for cell arrangement in an argon-filled glove box. A 14 mm diameter of a pure metallic sodium used as a reference material was carefully placed over a support of stainless-steel and rolled over a plastic foil to resist any form of circuit breakage. A glass microfiber filter (GF/A) paper of 14 mm diameter was used as separator, and sodium hexafluorophosphate ($NaPF_6$) was used as electrolytes. The whole settings was coupled as shown in Figure 20 in the glove box.

Figure 18: *Sodium (Na) battery cell development*

3.5.1.3 Electrochemical testing

Galvanostatic tests were carried out on a potentiometer (PARSTAT) operated by VersaStudio to analyse the charge and discharge performances of the different carbon electrodes over 10 cycles. The test was measured over a voltage difference of upper and lower limits of 3.4 V and 1 V, respectively between the two electrodes over time at a constant current of 20 µA. Four cells were made for each carbon electrode to ensure the reproducibility of the measurements. Iterations were performed on the upper and lower limit to generate the discharge and charge respectively. A measurement of cell stability expressed as coulombic efficiency along successive cycles was obtained through a ratio of discharge (de-insertion) and charge (insertion) and expressed as percentage. The capacitance was calculated from a ratio of discharge divided by the mass of carbon electrode.

3.5.2 Methylene blue dye absorption

Selected activated chars containing meso-macro pores produced where compared to activated chars of HTC. The main goal is to find application of the activated char for water treatment while also comparing the influence of activated chars with bigger pore development. To achieve this, 100 g of methylene blue dye was dissolve in 50 ml of water creating a concenterated dye solution. The activated char was then introduce into the aqueaous solution after it has been placed on a shaker and out reach of sunlight. Solution of the dye were then collected at diffrerent time intervak of 1, 2, 4, 6, 8, 10, 15, 20, 40, 60, 110, 150 and 300 minutes and stored for further analysis using the UV spectrometer and their absorbance were determined and recoreded. Images of collected samples is shown in the figure 19.

Figure 19: *Methylene-blue dye Absorption Experiment*

3.5.3 Other application as carbon stability in Pt/C ORR Catalysts

This study delves into the exploration of the efficacy of graphitization in enhancing the stability of activated carbon used as a catalyst support for Pt/C in the oxygen reduction reaction (ORR). Focusing on sustainable alternatives for catalysts within Proton Exchange Membrane (PEM) fuel cells, the activated char produced underwent a crucial step of thermal treatment at elevated temperatures up to 2800 °C under reducing conditions at 1100 °C. The primary objective was a systematic investigation into how these treatment parameters influence the surface and structural properties of the resulting carbon material. Employing various physical characterization methods, the treated activated char was meticulously analyzed. Subsequently, small Pt nanoparticles were deposited onto the activated char-based supports, creating catalysts active in the ORR. The performance of these novel catalysts underwent evaluation through thin-film rotating disc electrode measurements. To gauge their effectiveness, the ORR activity and stability of these catalysts were compared to a commercial Pt/C catalyst derived from raw oil. This research further explores the impact of support modification on ORR performance, shedding light on the potential application of activated char-based carbon materials as sustainable alternatives for Pt-based catalysts in PEM fuel cells. This investigation serves as a significant chapter in the broader application of the developed activated carbon, contributing to the development of environmentally conscious and sustainable solutions in the realm of energy production. The results obtained during this application is published and reported in the publications and conferences chapter.

3.6 Overall Experimental Summary

The overall experimental summary is given in Figure 20. This summary gives the general methodological process and analysis of this research.

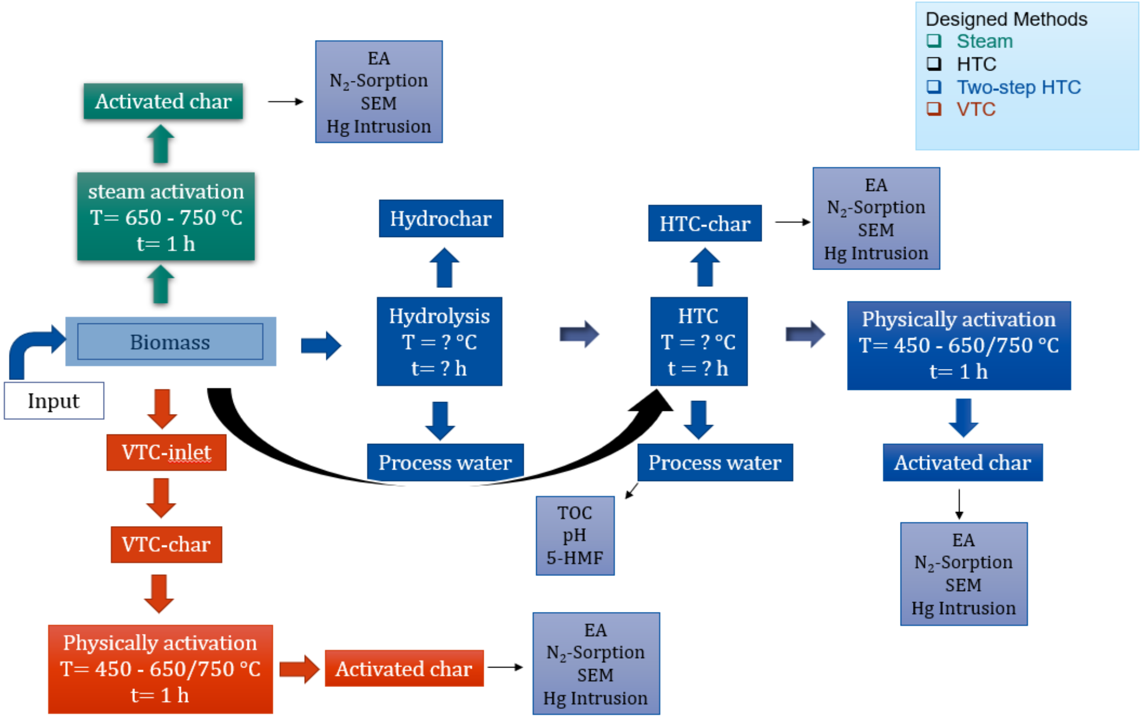

Figure 20: *Experimental Overview*

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

The presentation of results and subsequent discussion revolves around a methodological comparison of all pertinent approaches employed in this research. The overarching objective of this study is to engineer a waste-free technology. A key focus was placed on comparing the process water generated from hydrothermal carbonization (HTC) with that from the two-step HTC method, given that these methods result in process water generation, unlike steam activation (ST), vapourthermal carbonization (VTC), and pyrolytic carbonization (PYC).

Furthermore, a comprehensive analysis was conducted on chars and activated carbon produced through each method to assess which approach yields optimal results in terms of both quantity (yield) and quality (pore structures). This comparison is vital in determining the most effective and efficient method for achieving waste-free and sustainable technological processes.

4.1 Process Water Analysis

4.1.1 Effect of temperature and time on pH

The investigation into the influence of temperature and time on pH levels was conducted using a pH meter for each hydrothermal condition. The results were compared against the initial pH without carbonization, as indicated in Table 3 for standard HTC and Tables 4 and 5 for the two-step HTC method. In order to comprehend the impact of time, both short and long hydrolysis durations were considered for the two-step HTC, with their respective pH values presented in Tables 4 and 5.

Before undergoing HTC, the initial pH of poultry litters with a high proportion of sawdust (S67M33) was measured at 6.0, while other constituents with significant or equal amounts of chicken manure, such as S50M50 and S33M67, recorded pH values of 6.2. Sawdust and chicken manure only measured 4.4 and 6.3, respectively, showcasing their acidic nature of all starting material. Post-HTC treatment, it was observed that the pH of all poultry litters decreased from their initial values, rendering them more acidic. For instance, the pH of S67M33 became more acidic, dropping from 6.0 to approximately 4.3. This decline in pH can be attributed to substrate degradation during hydrothermal carbonization, leading to the formation of organic acids in the HTC process (Hendriks and Zeeman, 2009; Reza et al., 2015).

Similar pH trends were observed in the two-step HTC compared to the standard HTC method. However, a slight increase in pH was noted as the hydrolysis temperature was raised during the long hydrolysis duration in the two-step HTC. This phenomenon is likely due to the presence of ammonia (Mumme et al., 2011; Reza et al., 2016a) and the potential formation of acetic acid, causing the dissolution of certain mineral components in the feedstocks found in the process water (Bach et al., 2013; Kambo and Dutta, 2015; Ghanim et al., 2016).

Regardless of the HTC method employed (standard or two-step), the pH was found to be in equilibrium across various HTC conditions, with only minor variations observed in the pH of the long hydrolysis duration. Overall, the pH of poultry litters with a high proportion of sawdust (S67M33) was consistently observed to be 4.3, while poultry litters with a high amount of chicken manure (S33M67) registered a pH of 5.1 under various carbonization conditions.

Table 3: *pH investigation of Standard HTC*

Samples	*No HTC*	*Standard HTC Conditions*			
		200°C/2hrs	200°C/4hrs	220°C/2hrs	220°C/4hrs
S	4.4	3.0	3.0	2.9	2.9
S67M33	6.0	4.2	4.3	4.4	4.3
S50M50	6.2	4.6	4.9	4.9	4.8
S33M67	6.2	4.9	5.0	5.2	5.0
M	6.3	5.7	6.0	6.5	6.5

Table 4: *pH investigation of Two-step HTC with short hydrolysis duration*

Samples	*No HTC*	*Hydrolysis_HTC Conditions (Two-step HTC)*			
		HY_130°C/1hr HTC_200°C/3hrs	HY_130°C/1hr HTC_220°C/3hrs	HY_150°C/1hr HTC_200°C/3hrs	HY_150°C/1hr HTC_220°C/3hrs
S	4.4	3.0	2.9	2.9	2.8
S67M33	6.0	4.3	4.2	4.2	4.3
S50M50	6.2	4.5	4.7	4.5	4.7
S33M67	6.2	4.8	5.1	4.7	5.1
M	6.3	5.3	5.9	5.6	6.5

***Table 5:** pH investigation of Two-step HTC with long hydrolysis duration*

Samples	*No HTC*	*Hydrolysis_HTC Conditions (Two-step HTC)*			
		HY_130°C/3hrs HTC_200°C/1hr	HY_130°C/3hrs HTC_220°C/1hr	HY_150°C/3hrs HTC_200°C/1hr	HY_150°C/3hrs HTC_220°C/1hr
S	4.4	3.0	3.1	2.9	2.8
S67M33	6.0	4.8	4.3	4.7	4.3
S50M50	6.2	5.3	4.5	5.1	4.7
S33M67	6.2	4.9	4.8	5.2	5.1
M	6.3	5.4	5.2	5.7	6.5

4.1.2 Effect of reaction temperature and time on the Total Organic Carbon (TOC)

The investigation into the impact of reaction temperature and residence time on the total organic carbon (TOC) content in process water was carried out for both standard HTC (Table 6) and two-step HTC, with the results presented in Table 7 and 8. Notably, the total organic carbon present in the process water after HTC was found to be influenced by HTC conditions, including temperature and time. A key observation was that the TOC value in standard HTC exceeded that in two-step HTC is likely attributed to the replacement of fresh distilled water after hydrothermal pretreatment in the two-step HTC. Additionally, TOC was observed to increase with higher proportions of chicken manure in the poultry litters during both HTC and two-step HTC.

In standard HTC, an average TOC across all carbonization conditions for poultry litters with a high proportion of sawdust (S67M33) was 7.6 g/l, increasing to 9.6 g/l with a higher amount of chicken manure (S33M67), and averaging 8.6 g/l for S50M50 with equal amounts of sawdust and chicken manure. The study revealed that variations in temperature and time, specifically at 200 °C and 220 °C for 2 and 4 hours, were sufficient to extract organic carbon into the solution, reaching an equilibrium value. Increasing the temperature from 200 °C to 220 °C resulted in nearly equal amounts of organic carbon in the process water.

In the two-step HTC process, it was possible to reduce the TOC of S67M33 from an average value of 7.6 g/l to 6.8 g/l, indicating a slight reduction. Similarly, for other poultry litters such as

S50M50, the TOC was reduced from an average value of 8.6 g/l in HTC to 7.6 g/l in two-step HTC, while S33M67 saw a reduction from 9.6 g/l to 8.7 g/l. On average, a TOC reduction ranging from 0.6 to 1.0 g/l was observed with the implementation of two-step HTC compared to standard HTC. Furthermore, employing long-term hydrolysis in two-step HTC resulted in additional TOC reduction compared to short-term hydrolysis conditions in both two-step HTC scenarios. The average loss ranged from 0.1 to 0.7 g/l, attributed to water changes after long hydrolysis.

Given that the substantial amount of heavily polluted process water is a current drawback of hydrothermal carbonization technology, the modified two-step hydrothermal carbonization method provides a potential solution to mitigate the associated challenges and reduce environmental impact.

Table 6: *TOC of Standard HTC Conditions*

Samples	*TOC of Standard HTC Conditions (g/l)*				
	200°C/2hrs	200°C/4hrs	220°C/2hrs	220°C/4hrs	Average
S	7.4	7.4	7.3	6.8	7.2
S67M33	7.8	7.1	7.5	7.8	7.6
S50M50	8.6	8.5	8.5	8.9	8.6
S33M67	9.2	10.0	9.8	9.5	9.6
M	11.7	12.5	12.7	12.4	12.3

Table 7: *TOC of short term Hydrolysis Conditions (Two-step HTC)*

Samples	*TOC of short term Hydrolysis Conditions (Two-step HTC) g/l*				
	HY_130°C/1hr HTC_200°C/3hrs	HY_130°C/1hr HTC_220°C/3hrs	HY_150°C/1hr HTC_200°C/3hrs	HY_150°C/1hr HTC_220°C/3hrs	Average
S	8.6	8.7	8.7	9.1	8.7
S67M33	7.2	7.0	7.3	7.8	7.3
S50M50	7.9	7.3	7.5	7.6	7.6
S33M67	8.6	8.4	8.8	8.9	8.7
M	10.3	10.1	11.3	11.9	10.9

Table 8: *TOC of long term Hydrolysis Conditions (Two-step HTC)*

Samples	*TOC of long term Hydrolysis Conditions (Two-step HTC) g/l*				
	HY_130°C/3hrs HTC_200°C/1hr	HY_130°C/3hrs HTC_220°C/1hr	HY_150°C/3hrs HTC_200°C/1hr	HY_150°C/3hrs HTC_220°C/1hr	Average
S	9.0	9.6	7.4	7.5	8.3
S67M33	7.7	7.7	5.9	7.1	7.1
S50M50	8.1	8.2	5.7	8.0	7.5
S33M67	8.7	9.6	7.6	8.7	8.7
M	10.9	11.6	8.7	9.4	10.2

4.1.3 Effect of temperature and time on the production of 5-HMF

In the initial phase of the experiments, the impact of HTC reaction parameters, specifically temperature and time, on the production of 5-HMF was examined. To ensure method accuracy, the residence time was maintained at 4 hours for both standard and two-step HTC processes. The investigation revealed that HTC conditions significantly influenced the production and optimization of 5-HMF. When retention time was varied with temperature of 200 and 220 °C in standard HTC (Figure 21), the optimal 5-HMF production occurred at a short retention time of 2 hours. Conversely, with constant retention time and varying temperature in standard HTC, the optimal 5-HMF production was associated with a moderate temperature of 200 ℃. This suggests the thermal instability of 5-HMF, with the optimum HTC conditions for all poultry litters being 200 ℃ at 2 hours.

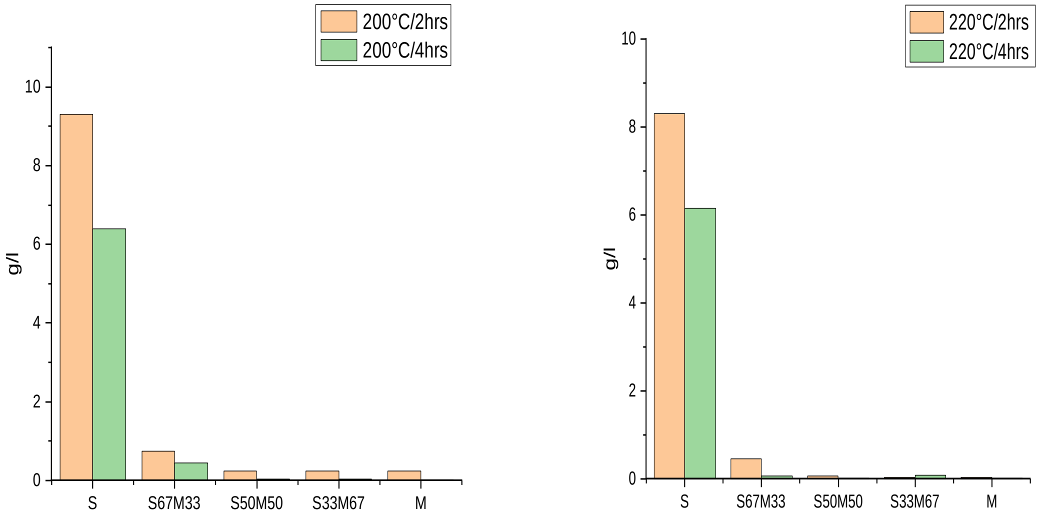

Figure 21: *5-HMF quantification at a different temperature of varying retention time*

The total 5-HMF produced at this optimal conditions (200 °C/2 hours) during standard HTC for sawdust was 9.2 gl^{-1}, and 0.74 gl^{-1} for poultry litter S67M33 containing a high amount of sawdust. Further reduction occurred to 0.25 gl^{-1} for poultry litter S50M50, and other poultry litters such as S33M67 and M showed negligible amounts.

However, 5-HMF optimization was possible using the modified two-step HTC conditions. The amount of 5-HMF achieved through the two-step HTC, resulted in increasing amounts for sawdust, S67M33, and S50M50 to 15.3 gl^{-1}, 1.88 gl^{-1}, and 0.4 gl^{-1}, respectively, compared to the 5-HMF of standard HTC values of 9.3 gl^{-1}, 0.74 gl^{-1}, and 0.25 gl^{-1}. Optimal 5-HMF production for sawdust, S67M33, and S50M50 occurred at reaction conditions of two-step HTC of HY_130/1hr_HTC_200/3hrs, HY_150/3hrs_HTC_220/1hr, and HY_130/1hr_HTC_200/3hrs, respectively (Figure 22 and 23). Prolonged pretreatment at temperatures above 150 ℃ resulted in reduced 5-HMF yields. It was also observed that short hydrolysis in the two-step HTC doubled 5-HMF production for sawdust and S50M50 from 9.3 to 15.3 gl^{-1} and 0.25 to 0.4 gl^{-1} respectively while longer hydrolysis optimized production of S67M33 from 0.84 to 1.88 gl^{-1}. In the two-step HTC, the separation of process water after pretreatment and addition of fresh distilled water mitigated the impact of poultry litters on 5-HMF optimization. The low 5-HMF content in chicken manure and other poultry litters with a high chicken manure proportion may be attributed to the composition of bacteria in the chicken's digestive system, which had facilitated the breakdown of the complex sugars, limiting the availability of glucose for 5-HMF production. Borda-Molina et.al, (2018) reported that in the digestive system of chickens, more than 900 bacteria is inhabited in their gastrointestinal tract (GIT) and these bacteria aid in the digestion of food. Clavijo and Flórez (2017) also reported that the commensal bacterial in the digestive system of the chicken contributes nutrients that are directly or indirectly needed to the chicken by hydrolysing all forms of complex sugars into primary sugars present in the chicken feed to aid in their rapid growth. From the reaction pathways as described by T.Wang et al., (2018), the production of 5-HMF can only be possible by the dehydration of glucose and since the chicken-manure is a bye-product of the chicken feeds which might contain little amount of glucose, this could therefore, justify the reason as to why the amount of 5-HMF in chicken manure or poultry litters with high amount of chicken manure is low.

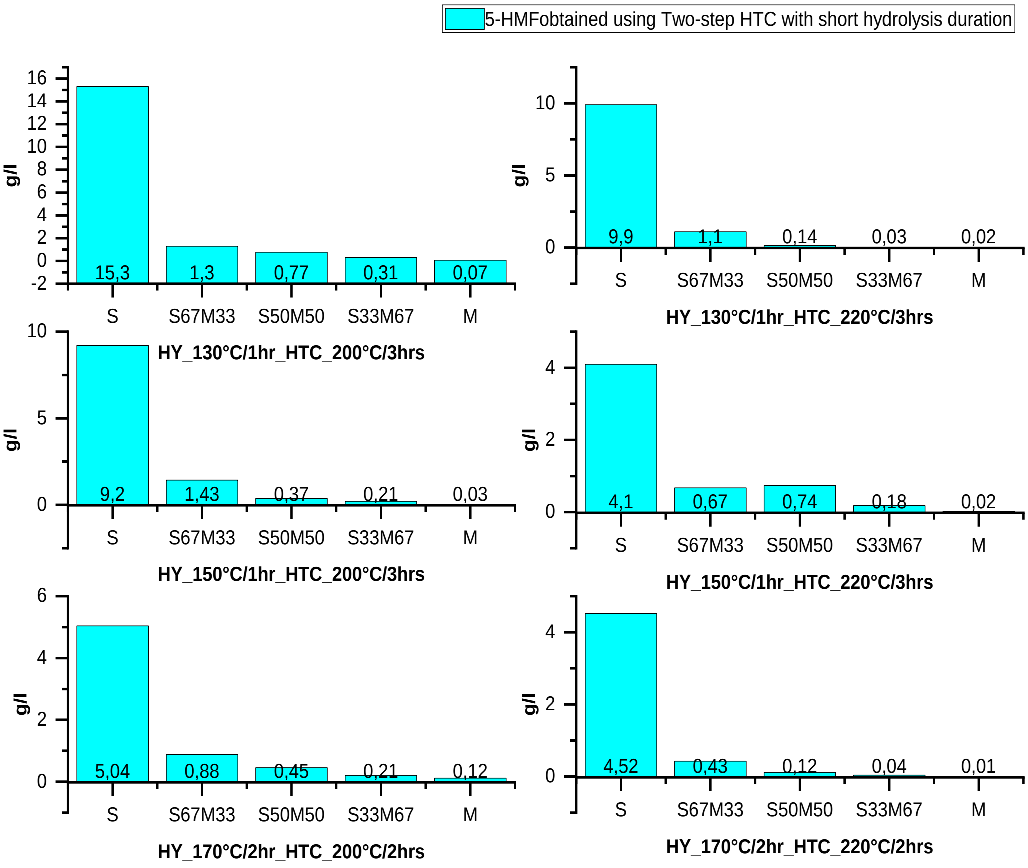

Figure 22: *5-HMF of two-step HTC conditions with short hydrolysis duration*

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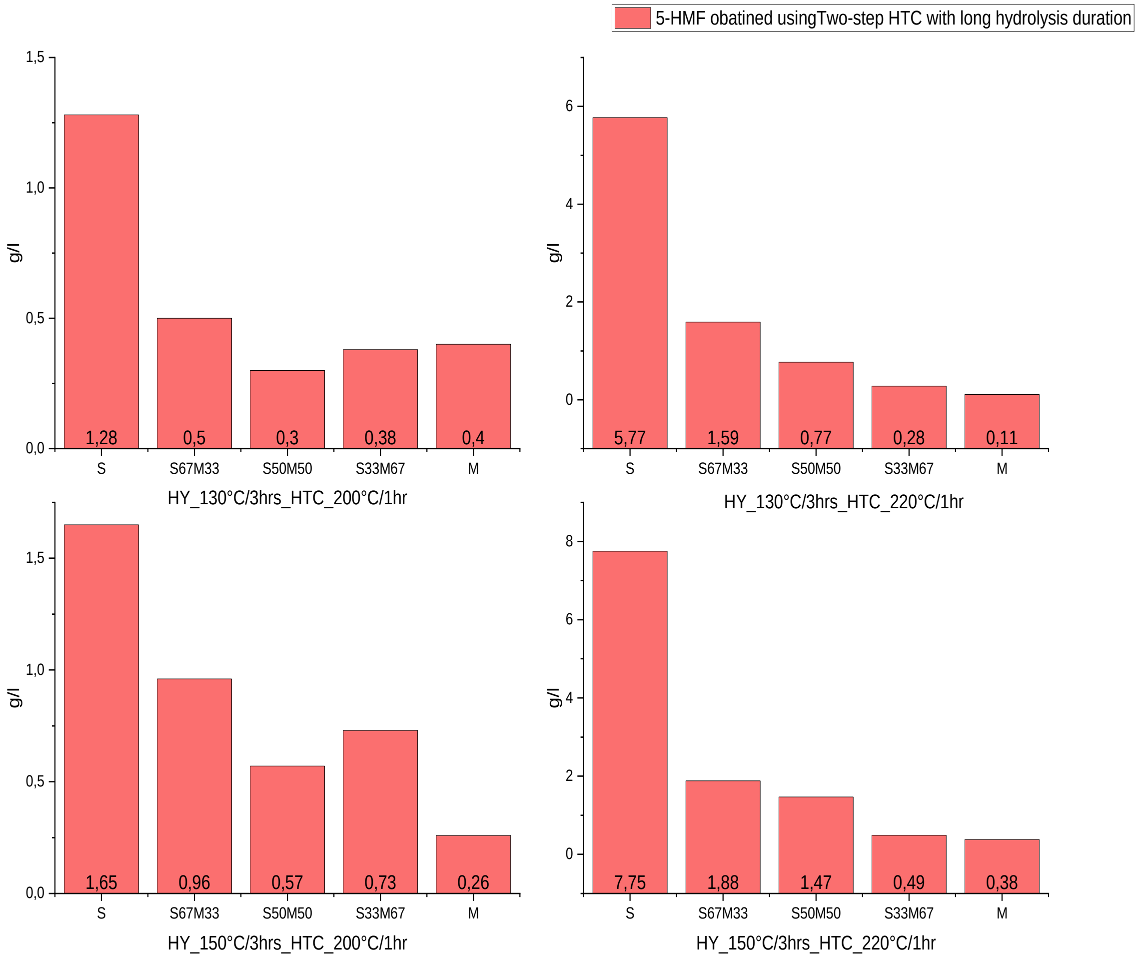

Figure 23: *5-HMF of two-step HTC conditions with long hydrolysis duration*

4.1.4 Algae degradation of the Total Organic Carbon in the process-water

Algae *Chlorella Vulgaris* was used for the waste-water treatment using an aquarium that is illuminated with LED-red (620 – 640 nm) and blue (430 – 490 nm). A 25:1 ratio of distilled water and HTC-water was used to guarantee optimal TOC degradation while its influence on algae growth was also evaluated. Each aquarium was loaded with 5 g of algae and 400 ml of diluted process water was used without adding any additional nutrients since HTC process waters often contain a large amount of nitrogen, phosphorus and a variety of organic compounds (McGaughy et al., 2019). During the cultivation, the TOC measurement was taken in short intervals at the beginning of the cultivation and longer at the end of the cultivation (Figure 23) which lasted for 30 days while the algae mass growth was recorded at the end of the experiment (Figure 24). It was observed that after 15 – 18 days the TOC degradations reach equilibrium and does not decrease any more. Similar results were reported by McGaughy et al (2019) and this might probably due to the algae fully degrading the organic compounds that are present in the process-water. The percentage amount of TOC degradation was observed to have declined after 18 days and this suggests the inadequate nutrients to sustain the algae while the slight decrease that occurs after 23 days may be due to the metabolic process of algae adapting to accommodate the decreased nutrients. The TOC of chicken manure was reduced to about 33 % and sawdust 18.7 % of its initial value while other poultry litters fall within the range of 18 – 33 % reduction as shown in Figure 24. At the end of the cultivation, the algae were separated from the process water via centrifuge at 4500 rpm for 10 minutes and their mass was measured, only as 'wet-weight'. It was observed that there was a mass loss when algae were used to degrade sawdust and little mass gain in chicken manure as compared to the excessive mass gain in the poultry litters. This could probably be due to the algae in a nutrient-rich environment such as process waters from poultry litters prioritizing growth of algae over nutrient uptake, while algae in nutrient-deficient environments such as process water from sawdust and manure prioritizing nutrient uptake before the growth of algae. The highest mass gain (23.95 %) in algae was obtained during process water treatment of poultry litters S67M33 (Figure 25).

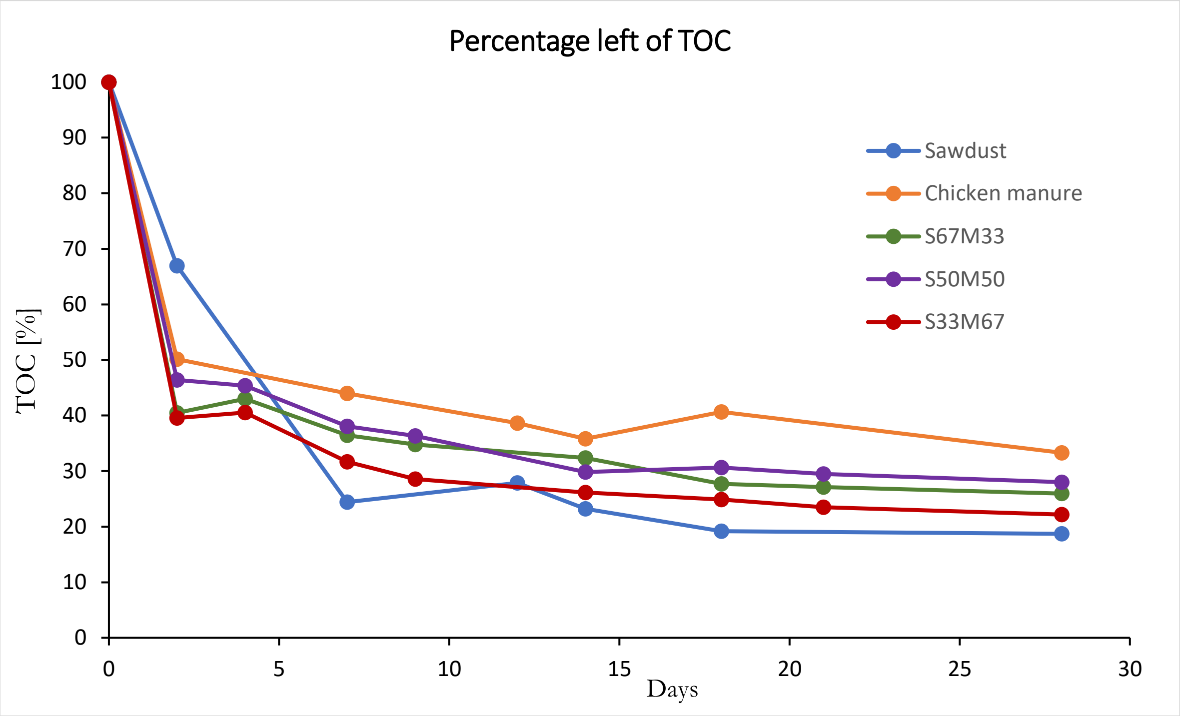

Figure 24: *TOC reduction of HTC process-water*

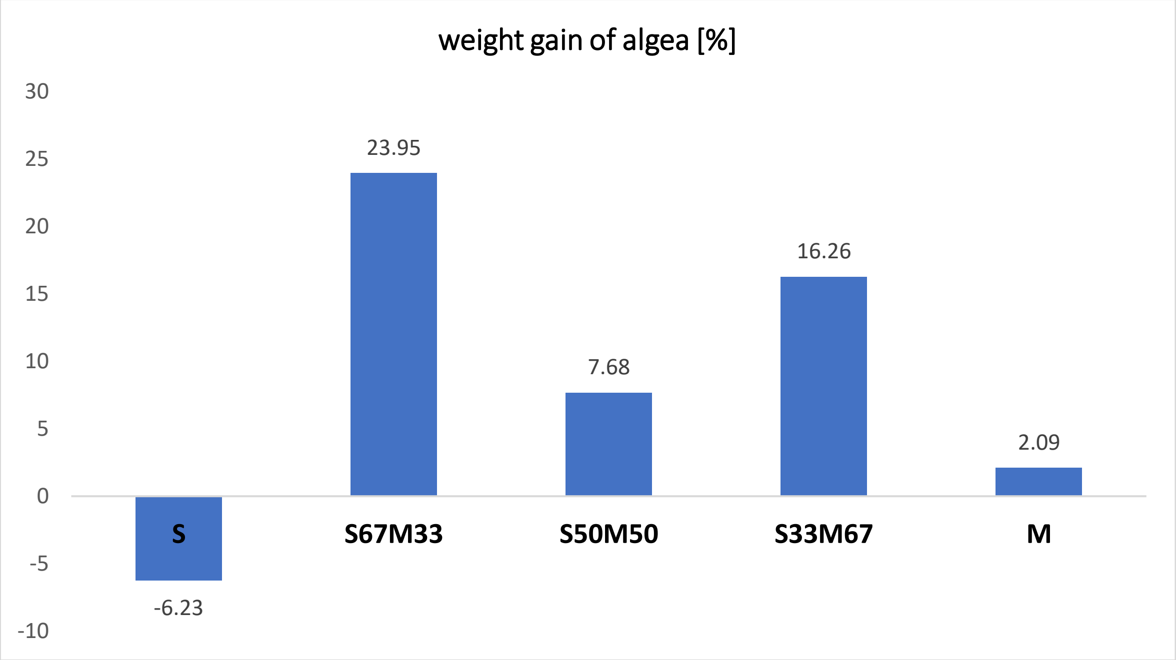

Figure 25: *Algae weight gain after TOC degradation*

4.2 Gas Chromatography (GC) Analysis

The amount of process gas generated in the reactor was determined and the result is presented in Figure 26 for sawdust and Figure 27 for chicken manure. For the gas collections, the reaction mixture was cooled to room temperature and the remaining process pressure, the free volume above the reaction mass and the temperature were collected into a gas sample holder. The percentage of carbon dioxide and methane in the process gas was determined using gas chromatography and It was observed that the amount of CO_2 by gas chromatography measurement (ϕCO_2 / %) for sawdust and chicken manure is 36.83 and 55.01 while the total amount of CH4 (ϕCH_4 / %) is 0.3 and 0.37, respectively.

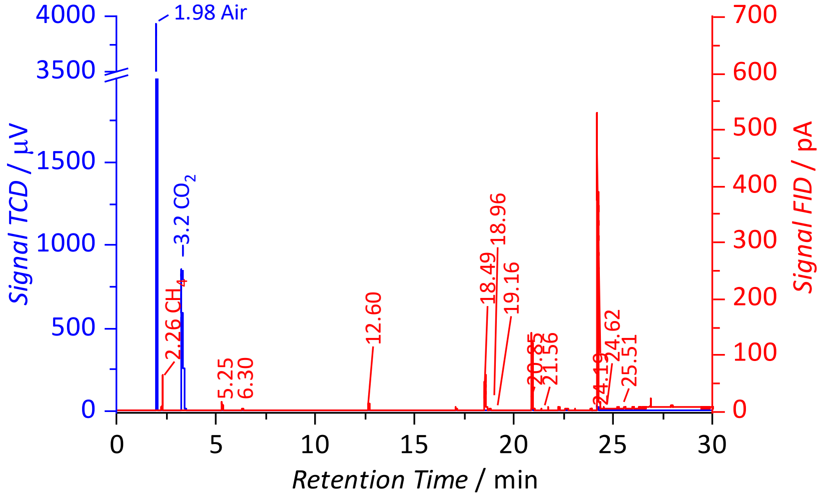

Figure 26: *GC-Analysis from HTC of Sawdust*

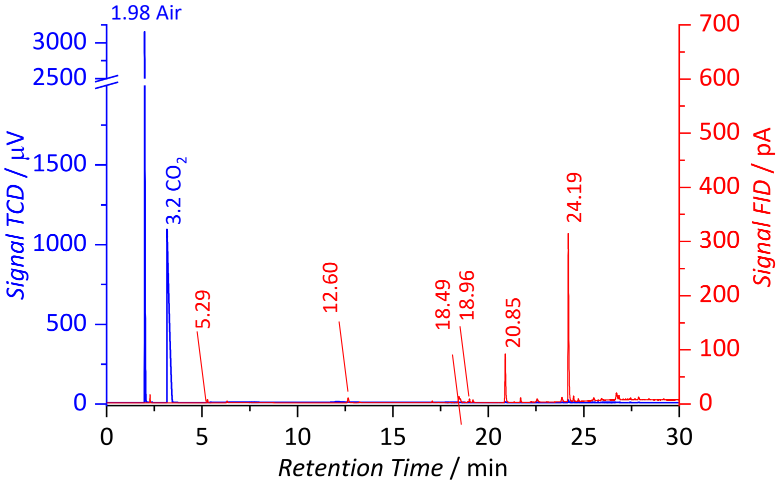

Figure 27: *GC-Analysis from HTC of chicken manure*

4.3 Char Analysis

Preceding the application of steam activation for the enhancement of the morphological structure, an examination was conducted on the hydrochar derived from hydrothermal carbonization (HTC) and the char from vapourthermal carbonization (VTC-char). The aim was to comprehend the impact of their thermal degradation processes utilizing water and vapour, respectively. Additionally, a more detailed analysis of the two-step HTC char focused specifically on the crystalline degradation of cellulose to produce 5-HMF, and this was compared with the characteristics of raw cellulose.

4.3.1 Scanning Electron Microscopy (SEM) of Hydrochar

The assessment of the fiber composition in the hydrochar, produced during hydrothermal carbonization (HTC), involved the acquisition and documentation of SEM images in this study. The SEM observations (Figure 28) revealed a well-defined surface on the produced hydrochars, attributable to the mild degradation of fiber components during the HTC process. The application of HTC facilitated a gentle treatment of biowaste, leading to nuanced thermal degradation and disintegration of its constituent fibers. Notably, the study aligns with the insights from Lynam et al. (2014), elucidating that within the structure of biowastes, lignin is predominantly located on the cell wall. The presence of a higher proportion of lignin, or the absence of other components, imparts a distinctive crusty texture to hydrochar. Therefore, the SEM findings in this investigation substantiate the fiber analysis, indicating that the hydrochars predominantly consist of pseudo-lignin and extractives. This outcome further explains the effectiveness of HTC in preserving the structural integrity of lignin-rich components during the hydrochar production process.

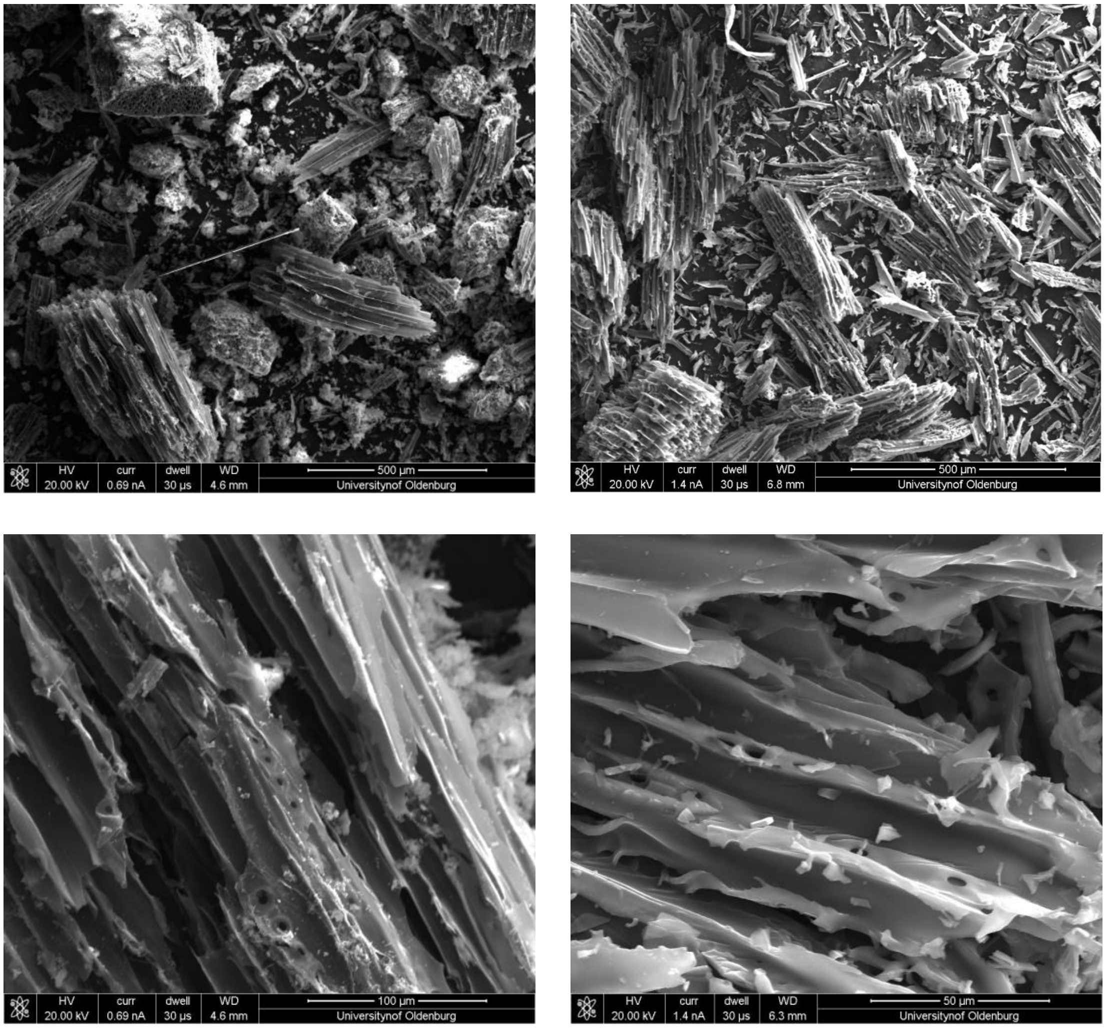

Figure 28: *SEM images of hydrochar (S50M50)*

4.3.2 Scanning Electron Microscopy (SEM) of VTC-char

In the examination of biowaste decomposition during vapourthermal carbonization (VTC), this study employed SEM imaging to meticulously scrutinize and report on the distinctive characteristics observed in VTC-char. The SEM observations unveiled a discernibly well-defined surface in the produced VTC-char, a manifestation attributed to the degradation of fiber components under the influence of vapour. The analysis delved into the intriguing revelation that the utilization of vapour not only facilitated decomposition but also contributed to the creation of intricate pores within the structural framework of VTC-char. The detailed SEM images (Figure 29) further illustrate the pronounced impact of vapour in inducing porosity, revealing a notable tendency to form larger pores compared to the more gently evolving structures observed in alternative synthesis methodologies. This visual evidence provides valuable insights into the intricate relationship between vapourthermal decomposition and the resulting microstructural features of VTC-char. Such findings contribute to a deeper understanding of the synthesis processes, emphasizing the unique influence of vapour in shaping the characteristics of carbonized materials.

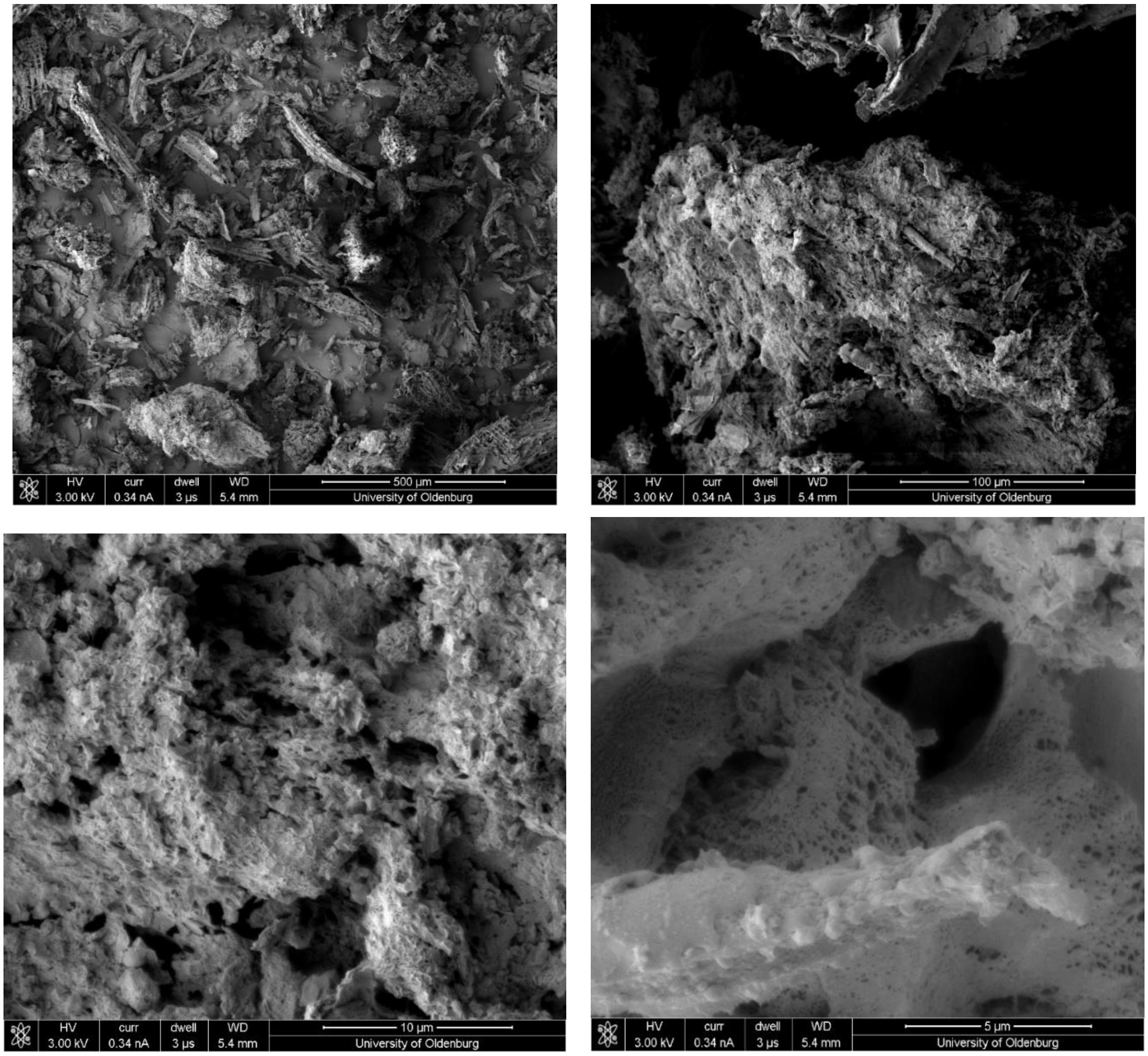

Figure 29: *SEM images of VTC-char (S50M50)*

4.3.3 X-Ray Diffraction (XRD) Analysis of hydrochar and VTC-char

The broad X-ray reflexes shown in Figure 29 observed at 2θ values approximately around 15°, 22°, and 35° are indicative of the characteristic assignments of 110, 200, and 004 planes in the crystalline cellulose, respectively. Notably, these reflexes undergo discernible changes during both hydrothermal carbonization (HTC) and vapourthermal carbonization (VTC) processes, attributed to the removal of amorphous compounds such as hemicelluloses. In the case of HTC, a notable reduction or disappearance of these reflexes is evident. This phenomenon implies a degradation of crystalline cellulose, signifying the influence of water used during the process. The diminished reflexes explains the impact of hydrothermal conditions in promoting the breakdown of the crystalline structure, particularly under the influence of water. Conversely, the XRD pattern for VTC presents a distinct profile with several reflexes at various 2θ values. This characteristic pattern indicates the non-degradation of cellulose during VTC, attributed to the use of vapour. The inability of vapour to degrade cellulose is manifested in the preservation of multiple reflexes, signifying the resilience of the crystalline cellulose structure under these conditions.

This XRD analysis (Figure 30) provides valuable insights into the structural changes during HTC and VTC, highlighting the distinct roles of water and vapour in influencing the crystalline integrity of cellulose in the respective carbonization processes.

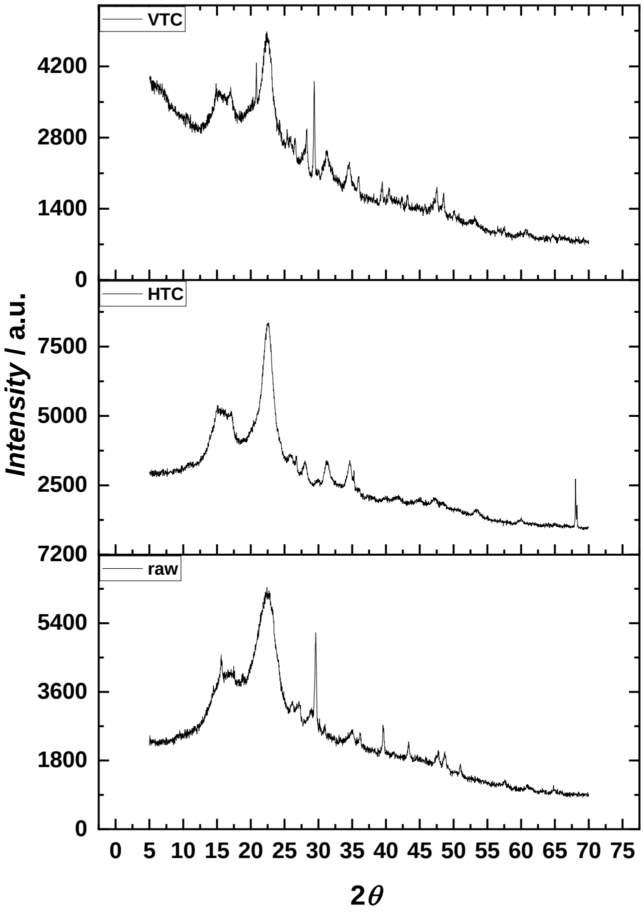

Figure 30: *XRD analysis of hydrochar and VTC-char*

4.3.4 X-Ray Diffraction (XRD) analysis of Two-step HTC

The XRD analysis of char produced from 2-step Hydrothermal Carbonization (HTC) process aimed to provide a deeper understanding of biowaste decomposition, as depicted in Figure 31. The results indicate that the broad x-ray reflexes at 2θ values around 15°, 22°, and 35° correspond to characteristic assignments of 110, 200, and 004 planes in crystalline cellulose, respectively. These reflexes show significant variations after HTC, particularly post 4 hours, attributed to the removal of amorphous compounds like hemicelluloses.

In the case of HTC after 12 hours, the XRD pattern reveals a substantial disappearance of reflexes, signifying the degradation of crystalline cellulose under these conditions. Interestingly, despite the extended treatment duration of 12 hours, no detectable 5-HMF was observed in the process water. Moreover, at longer reaction times beyond 4 hours, a decline in the production of 5-HMF was noted, even in the absence of complete degradation of crystalline cellulose (Figure 31). This observation suggests that 5-HMF exhibits decreased thermal stability with prolonged reaction times. The result suggested that, through a gentle treatment approach facilitated by the two-step HTC process, it becomes possible to optimize the production of 5-HMF. The observed relationship between reaction time, crystalline cellulose degradation, and 5-HMF production underscores the potential for tailoring reaction conditions to achieve desired outcomes in the HTC process. This analysis contributes to a comprehensive understanding of the interplay between treatment parameters and the resulting structural and chemical transformations in the biowaste conversion process.

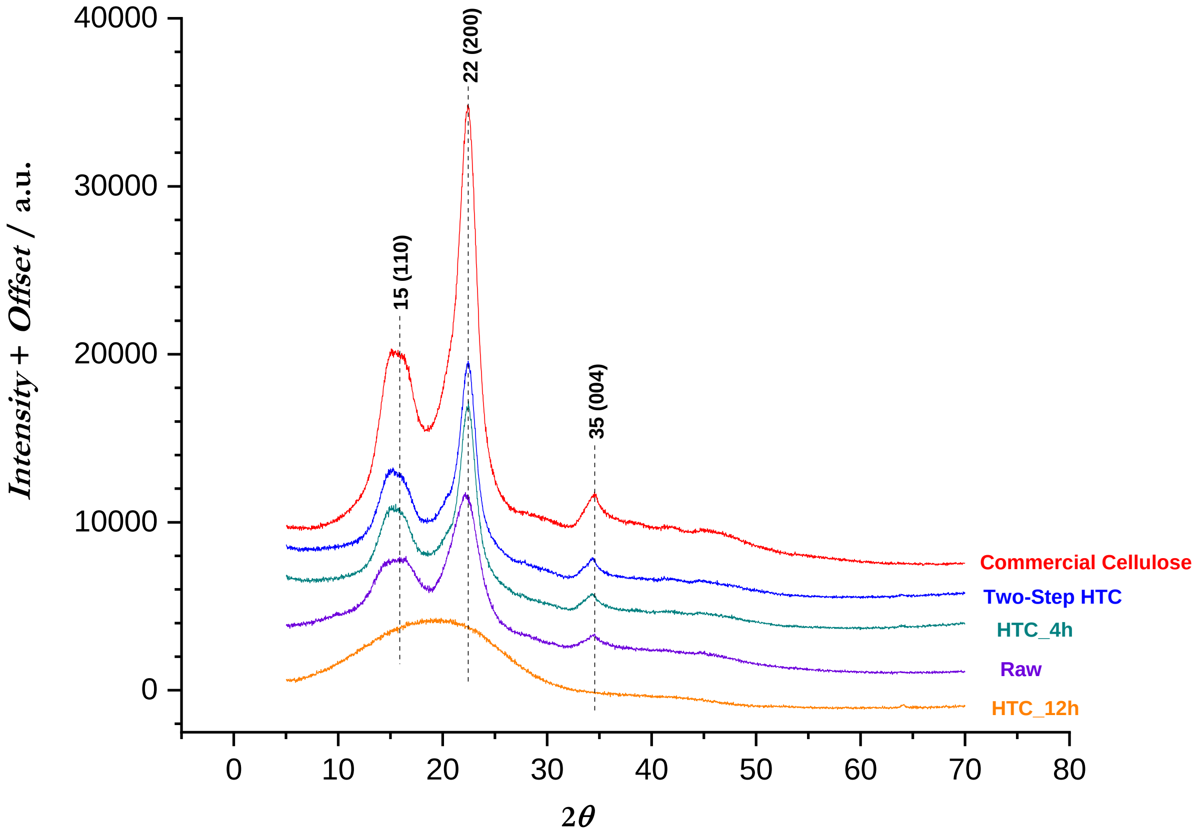

Figure 31: *Cellulose degradation in two-step HTC*

4.4 Analysis of HTC-activated chars

4.4.1 Nitrogen Sorption analysis of HTC-activated carbon

Hydrochars produced from HTC generally consist of small specific surface areas (SSA) and oxygenated functional groups (Saha and Reza, 2019). Considering the desired application fields to which the hydrochars are to be applied such as a sorbent for purifying wastewater and atmospheric air, or as conducting catalyst support in electrochemistry, there is a need for the enlargement of its surface area. Thus, this enlargement can only be achieved by activation processes such as steam, acidic or alkali. Due to the demerits associated with chemically activated chars (acidic and alkali) such as retaining the traces of the activated agents that are responsible for surface oxidation, physical activation by steam at a temperature of 650 °C at 1 hour was considered in this study. Nitrogen sorption was performed to evaluate the surface area, pore volumes and to understand the morphology of all the activated hydrochars produced using the standard HTC. The results indicated that activated hydrochar produced using the standard HTC method resulted in highly mesoporous and it is influenced by the amount of chicken manure in the PL. It was realised that in standard HTC, poultry litters at HTC condition of 220 ℃/2 hours is sufficient to produce activated hydrochars with high specific surface area. This HTC condition was observed to be common for all poultry litters regardless of the amount of ratio of sawdust to chicken manure. These results also show that as the amount of sawdust present in the poultry litters is increased from S33M67 to S67M33, so does the specific surface area is increased from 279 – 460 m^2/g (Table 9). However, this thus leads to the development of activated hydrochars with micropores as it was observed that chicken-manure contributes to the development of mesoporous in the poultry litters (Figure 6). The amount of mesoporous produced in the poultry litters decreases as the amount of sawdust is increased and this probably due to the high amount of inorganic present in the chicken manure. While it was observed that, hydrochars produced from sawdust has a high surface area (650 m^2/g) as compared to chicken-manure (420 m^2/g), the surface area was observed to reduce as the percentage of chicken-manure is increased in the poultry litters and this is due to the high ash content present in the chicken-manure after activation (Table 9). It was realised that the properties of hydrochar produced from sawdust were leading to microporous while chicken-manure was resulting in the development of mesoporous, therefore the amount of micro to meso pore volumes in the poultry litters were characterised, and the result is presented in Figure 32 – 36. The amount of mesopores volume was observed to have increased as the ratio of chicken manure is increased in the poultry litters which further indicates that chicken-manure is highly contributing to the development of the mesoporous.

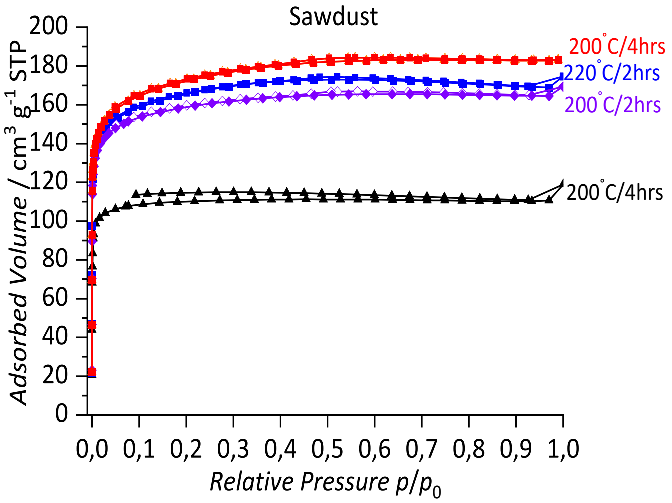

Figure 32: *Isotherm of activated carbon produced from sawdust via HTC*

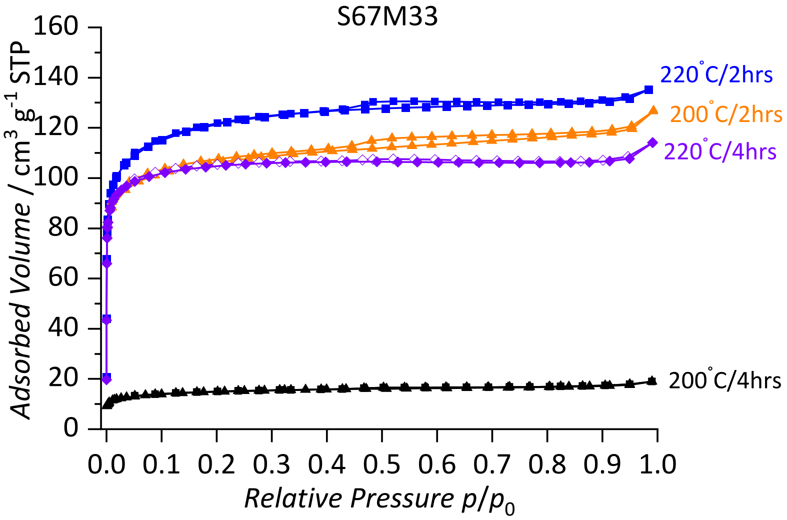

Figure 33*: Isotherm of activated carbon produced from S67M33 via HTC*

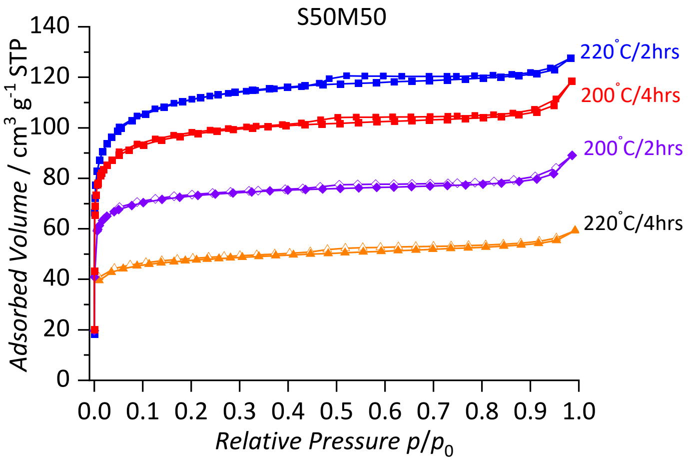

Figure 34: *Isotherm of activated carbon produced from S50M50 via HTC*

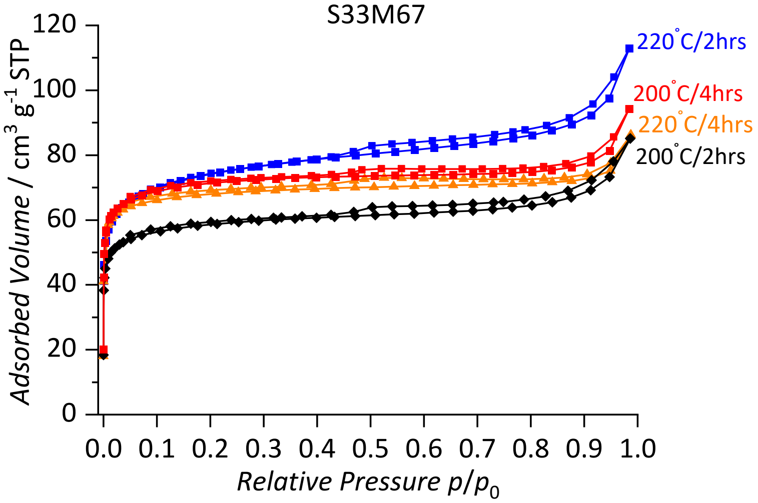

Figure 35: *Isotherm of activated carbon produced from S33M67 via HTC*

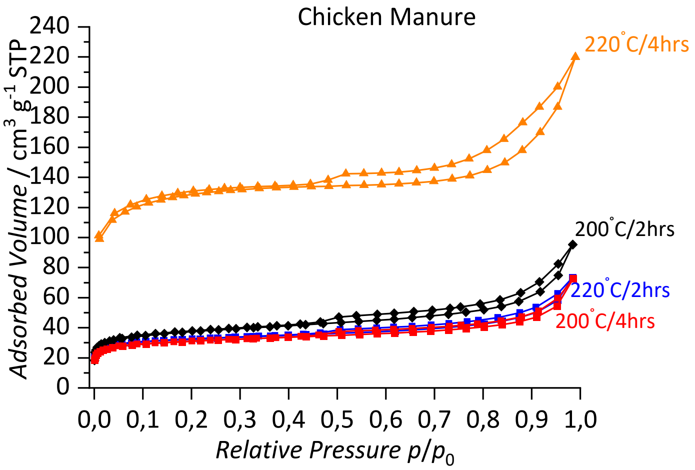

Figure 36: *Isotherm of activated carbon produced from Chicken Manure via HTC*

Table 9: *BET analysis of activated carbon with subsequent activation at 650 °C for 1 h via HTC*

Sample	**HTC conditions**		**SSA (m^2g^{-1})**	**PV (cm^3g^{-1})**
	Time (h)	**Temperature (° C)**		
Sawdust	2	200	619	0.255
		220	638	0.276
	4	200	660	0.283
		220	503	0.201
S67M33	2	200	413	0.174
		220	460	0.209
	4	200	55	0.029
		220	414	0.167
S50M50	2	200	283	0.137
		220	419	0.197
	4	200	374	0.182
		220	183	0.068
S33M67	2	200	227	0.130
		220	279	0.173
	4	200	279	0.145
		220	269	0.131
Chicken Manure	2	200	138	0.145
		220	122	0.112
	4	200	116	0.101
		220	488	0.340

4.4.2 Yield analysis of HTC-activated carbon

The examination of hydrochar yield following Hydrothermal Carbonization (HTC) and subsequent activation is outlined in Figure 37. Post-HTC, a reduction in mass was observed, attributed to the biomass constituents entering the solution under thermal conditions. Notably, there was a modest loss in yield during the subsequent activation to produce activated char. Following HTC, a yield of 63 % was recovered, and after subsequent activation at 650 °C, a total yield of 52 % was obtained. This post-HTC analysis underscores the thermal stability of the activated char, a characteristic attributed to its initial treatment via Hydrothermal Carbonization. These results shed light on the dynamic changes in yield through the HTC and activation processes, offering insights into the transformation of hydrochar under different thermal treatments.

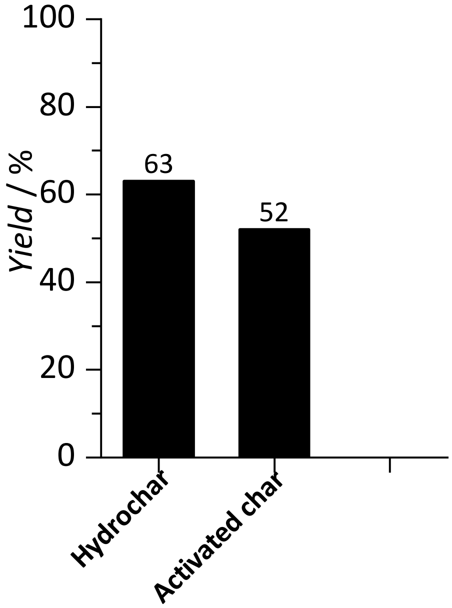

Figure 37: *Yield analysis of hydrochar and activated hydrochar*

4.4.3 SEM analysis of HTC-activated carbon

The investigation of activated HTC-char at 650°C through Scanning Electron Microscopy (SEM) imaging unveiled crucial insights into the resulting activated char's pore structure. The SEM findings indicate the transformative impact of the activation process on the pore characteristics of the material. Specifically, there is an observable enhancement in the pore size compared to the initial HTC-char. Figure 38 visually demonstrates the presence of pores on the surface of the activated HTC-char. However, it is imperative to note that these pores exhibit a non-uniform distribution and are not significantly enlarged. This nuanced observation can be attributed to the gentle treatment applied to the feedstock before activation. The SEM images suggest that the initial HTC treatment lays the foundation for the subsequent activation process, influencing the resulting pore structure. In support of these observations, relevant literature highlights the sensitivity of pore development in activated chars to precursor material properties and activation conditions. In summary, the SEM analysis of activated HTC-char at 650°C provides valuable visual evidence of changes in pore structure, reinforcing the potential of the activation process to influence the mesoporous characteristics of the material. The non-uniformity and limited enlargement of pores, attributed to the gentle HTC pre-treatment, explains the intricate relationship between precursor treatment and subsequent activation outcomes.

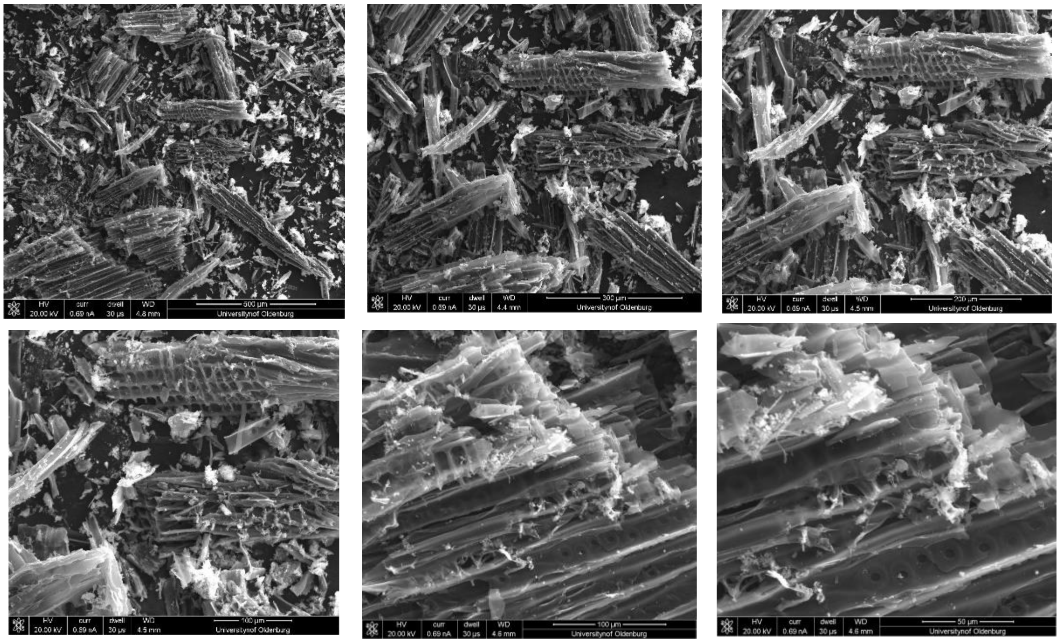

Figure 38: *SEM images of activated hydrochar (S50M50)*

4.5 Analysis of VTC-activated chars

4.5.1 Nitrogen Sorption VTC-activated chars

The quantification of process water for the amount of 5-HMF present from VTC proved challenging due to its inherent nature of vapour; nevertheless, the activated chars derived from it underwent additional steam activation, allowing for the analysis of their surface areas and pore structures. In the investigation, carbonization temperatures of 200 and 220 °C, coupled with retention times of 2 and 4 hours, were explored for poultry litters of S67M33 (Figure 39) and

S50M50 (Figure 40), guided by resource availability. The outcomes mirrored those observed for VTC-treated biomass, revealing heightened hysteresis at increasing relative pressure. This phenomenon signifies the influence of vapour penetration into the porous structure of the biomass material, particularly as the retention time increases.

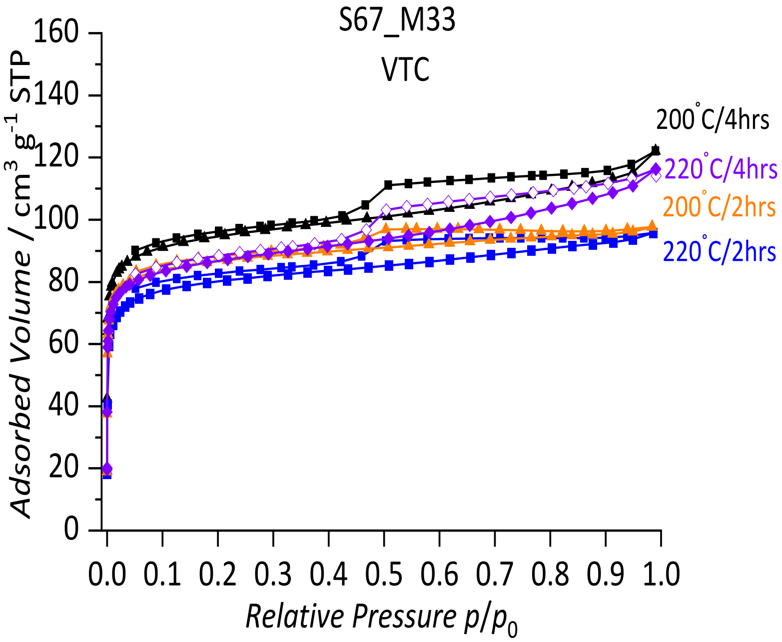

Figure 39: *Isotherm of activated carbon produced from S67M33 via VTC*

Activated chars generated through VTC exhibited discernible hysteresis patterns with increasing carbonization time. Notably, at both 200°C and 220°C, a more pronounced hysteresis was evident at 4 hours compared to 2 hours for both carbonization temperatures. Across various poultry litter mixtures, S50M50 displayed clearer hysteresis patterns associated with mesopores. Furthermore, an intriguing observation emerged at an increase in retention time from 2 to 4 hours corresponding to a broadening of pore sizes.

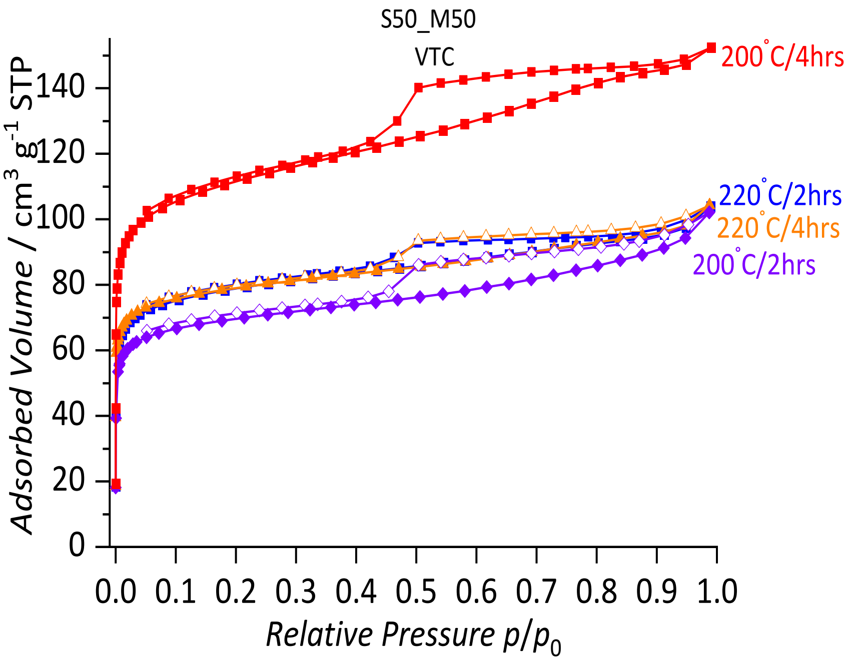

Figure 40: *Isotherm of activated carbon produced from S50M50 via VTC*

4.5.2 Yield analysis of VTC-activated chars

The evaluation of VTC-char yield after vapourthermal carbonization (VTC) and subsequent steam activation is presented in Figure 41. Following VTC, a marginal yield loss was observed, attributed to the influence of vapour. This outcome suggests the absence of biomass constituent decomposition in the vapour phase, resulting in an impressive average yield recovery of 98 %. However, during the subsequent activation process, the average yield notably decreased to 38 %, indicating a substantial loss in mass. This significant reduction is attributed to the inherent instability of the char structure, which undergoes oxidation and dissipates into the atmosphere during the activation stage. The distinct yield variations after-VTC and activation underscore the transformative impact of activation treatments on VTC-char composition and stability.

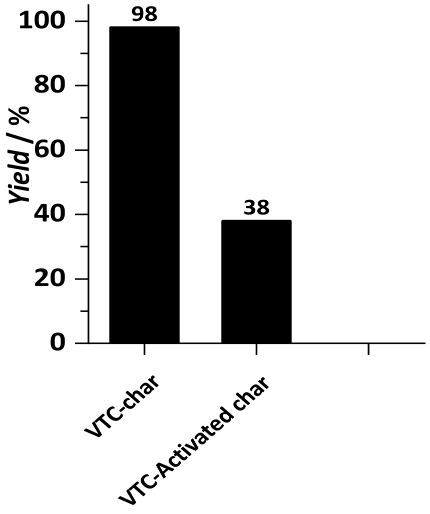

Figure 41: *Yield analysis of VTC-char and activated VTC-char*

4.5.3 SEM analysis of VTC-activated carbon

The investigation of activated VTC-char at 650 °C via SEM imaging provided valuable insights into the pore structure of the resulting activated char. The findings suggest that the activation process has the potential to augment the pore size of VTC-char significantly. Notably, Figure 42 illustrates the presence of larger pores on the surface of the activated VTC-char. The observed increase in hysteresis with rising relative pressure during nitrogen sorption analysis aligns with the SEM results. This correlation supports the contention that activated char produced through vapour thermal carbonization (VTC) exhibits a heightened level of mesoporosity. The SEM observations affirm the efficacy of the activation process, leading to the production of highly mesoporous char. This outcome underscores the promise of vapour thermal carbonization, coupled with subsequent enhancements, in yielding materials with enhanced mesoporous activated char production.

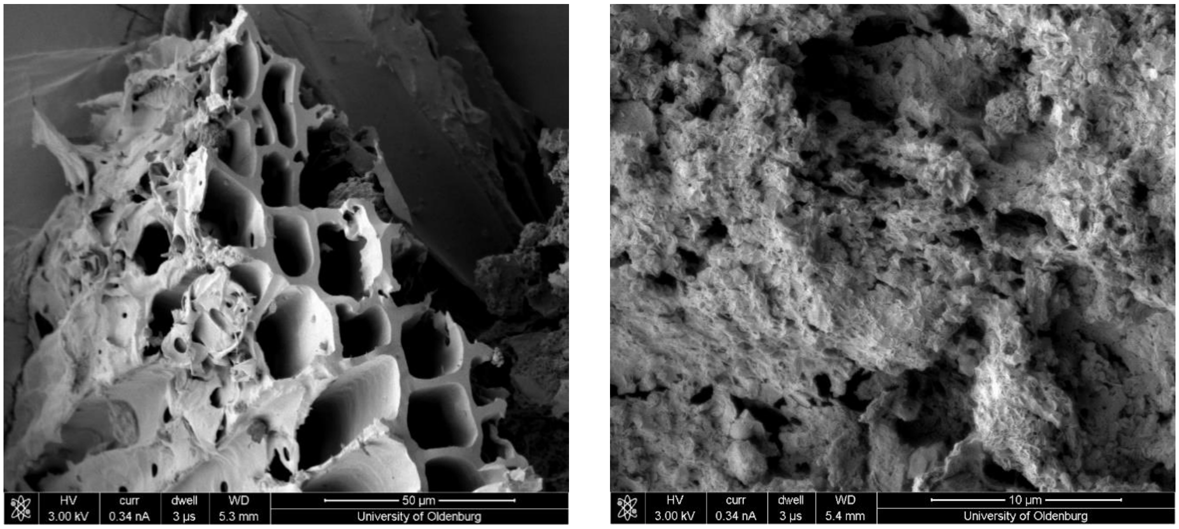

Figure 42: *SEM images of activated VTC-char (S50M50)*

4.5.4 Mercury (Hg) Intrusion analysis of VTC-activated chars

In light of the abundant mesopores evident in the SEM images of the activated VTC-char, a further analysis involving mercury intrusion porosimetry was conducted to further elucidate the pore structure of the activated char. The results of the mercury porosimetry revealed activated VTC-char contains a pore volume of about 0.1 cm^3g^{-1}. This thorough porosimetry analysis provides valuable insights into the diverse pore structures present in the activated VTC-char, offering a quantitative assessment of macropores, mesopores, and micropores.

4.6 Analysis of ST-activated chars

4.6.1 Nitrogen Sorption Analysis of ST

Nitrogen adsorption was performed to evaluate the specific surface area (SSA), pore volume (PV) and to understand the morphology of the carbon materials produced via steam. This method involves the direct activation of untreated biomass (poultry litters) resulting into activated carbon. The morphology of the activated carbon produced after subsequent activation of sawdust at 650 °C, 750 and 800 is shown in Figure 43 and labelled S650, S750 and S800 respectively. The results showed that a temperature of 650°C were resulting in activated carbon which contains mainly micropores. A further increase in temperature above 650 to 750°C led to carbon with a high amount of mesopores and surface area.

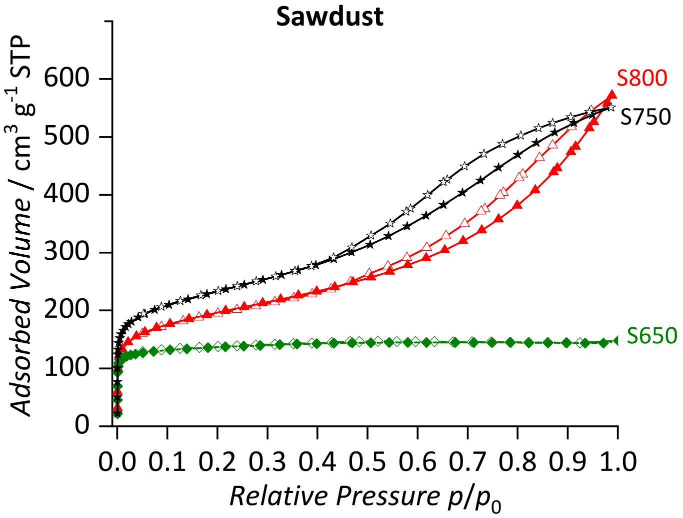

Figure 43: *Isotherm of activated carbon produced from sawdust via steam at a higher temperature*

However, poultry litters containing sawdust and chicken manure mixed in different proportions such as S67M33 and S50M50 and treated at a steam treatment of 750°C for the production of activated carbon. The result showed that a high amount of sawdust in the poultry litters resulted in carbon with high amounts of mesopores. Also, the treatment of pure chicken manure showed a reduction in the pore structure.

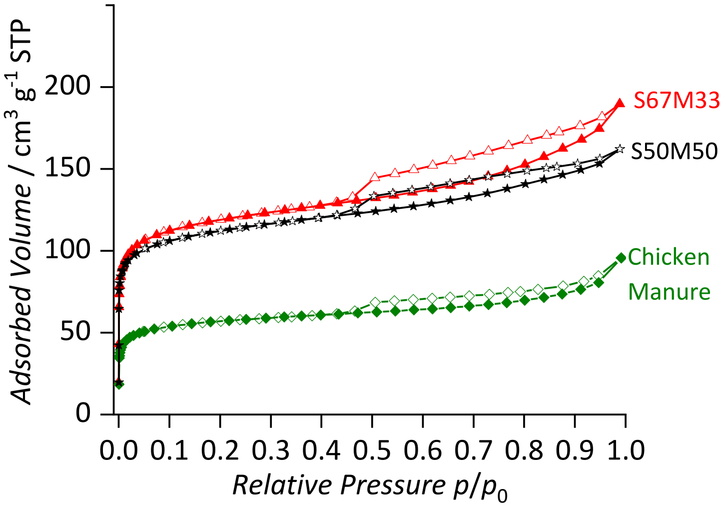

Figure 44: *Isotherm of activated carbon produced via steam*

While a high amount of chicken manure in PL was observed to contribute to the development of mesoporous carbon in HTC, the opposite was observed when PL was treated using steam at a high temperature (ST). The results indicate that PL with a high amount of sawdust influences the SSA, PV and pore distribution of the carbonaceous material. It was realised that during treatment via ST, a temperature > 650 °C was required to put out the organic compounds present in the PL which in turn leads to the production of carbon material with a large amount of mesopores and carbon deposit. Steam at high temperature was experimented for sawdust at 650, 750 and 800 °C to understand the influence of temperature in the production of activated carbon. The results indicated that it was possible to produce high amounts of mesoporous using a temperature of >650°C as shown in Figure 30.

Table 10: *BET analysis of activated carbon with subsequent activation at 650 °C for 1 h via HTC*

Sample	Temperature (°C)	Time (h)	SSA (m^{2}g^{-1})	PV (cm^{3}g^1)
Sawdust	650	1	530	0.220
	750	1	821	0.917
	800	1	706	0.870
2S:1M	750	1	424	0.248
1S:1M	750	1	449	0.290
Chicken Manure	750	1	216	0.143

4.6.2 Yield analysis of ST-activated chars

The assessment of yield for activated char, synthesized under conditions involving high temperatures and steam (ST), is a pivotal aspect of this study, and the detailed findings are visually represented in Figure 45. The outcomes highlight a noteworthy and considerable loss in yield, with an average of 18 % observed post-treatment. This substantial reduction in yield signifies a significant transformation during the synthesis process. The underlying cause of this substantial loss in yield can be traced to the oxidation of untreated biowaste under the rigorous conditions of elevated temperatures and steam. The untreated biowaste, when subjected to these conditions, undergoes a transformative process wherein its inherent structure becomes increasingly unstable and susceptible to oxidation. The intricate interplay of steam at high temperatures induces a pronounced alteration, leading to the observed loss in yield. This outcome justifies the sensitivity of the biowaste structure to the synthesis conditions, shedding light on the dynamic nature of the activation process under steam at high-temperature.

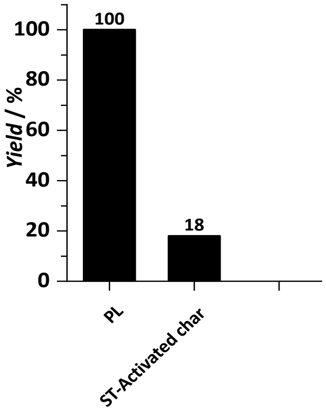

Figure 45: *Yield analysis of activated ST-char*

4.6.3 Mercury (Hg) Intrusion analysis of ST-activated chars

In light of the abundant mesopores evident in the activated ST-char (S750), a comprehensive analysis involving mercury intrusion porosimetry was conducted to further elucidate the pore structure of the activated char. The results of the mercury porosimetry revealed substantial macropore volumes in the micro-meso-macro-porous activated ST-char, as illustrated in Figure 46. The detailed findings indicate that the activated ST-char especially ST exhibits a significant macropore volume, measuring approximately 6.48 cm^3g^{-1}. Furthermore, the initial mesopores volume was determined to be 0.80 cm^3g^{-1}, and the micropores volume was found to be 0.07 cm^3g^{-1}, as depicted in Figure 46. The cumulative effect of these varied pore sizes contributes to a total pore volume of 7.30 cm^3g^{-1}. This thorough porosimetry analysis provides valuable insights into the diverse pore structures present in the activated ST-char, offering a quantitative assessment of macropores, mesopores, and micropores. Such detailed information is crucial for understanding the material's porosity and has implications for its potential applications in various fields.

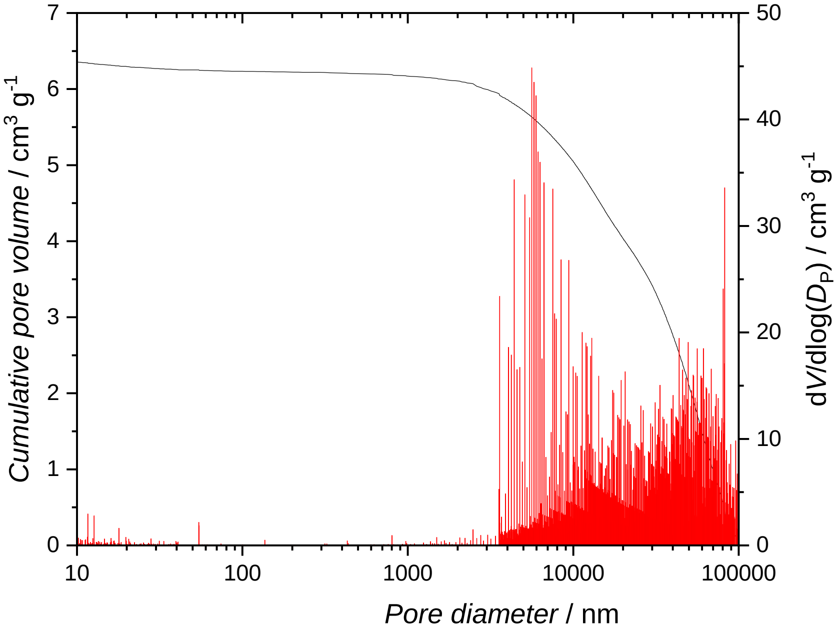

Figure 46: *Mercury porosimetry test of ST-activated char (Sawdust)*

4.6.4 ATR-FTIR activated chars

The structural characteristics analysis of one of the activated chars was undertaken, and the findings were compared to the raw poultry litter (PL) used in this study, despite the activated char having a similar Fourier Transform Infrared (FTIR) spectrum. The results, as depicted in Figure 47, revealed several distinctive features. A broad band at 3339 cm^{-1}, assigned to the stretching of OH bonds in water, carboxyl, and phenolic groups like aliphatic hydroxyl groups (Sun et al., 2000), was observed. This band exhibited a decrease in intensity in the activated char compared to the raw sample. This decline is attributed to the increased overall carbon content and the loss of polar surface functional groups, enhancing the hydrophobicity of the activated char and concurrently reducing wettability. At 1644 cm^{-1}, the bending vibration of adsorbed water in poultry litter was evident, but this signal was notably absent in the activated char (Figure 47). The aliphatic -CHx stretching vibrations of cellulose, hemicellulose, and lignin, found in the range of 2958 – 2857 cm^{-1} (Sun et al., 2000), exhibited a significant increase in intensity for the activated char compared to the raw sample. Carbonyl stretching vibrations of hemicellulose and lignin, located at 1732 $cm^{-1}$and 1698 cm^{-1}, associated with ketones, carboxyl acidic esters, and anhydrides (Egües et al., 2013), were identified. These signals demonstrated noticeable changes, further emphasizing the impact of carbonization on these functional groups. The intense signals at 1057 cm^{-1} and 1033 cm^{-1} in the raw sample's spectrum indicated C–O stretching vibrations in polysaccharides, particularly in ether and hydroxyl groups. However, the intensity of these bands decreased after carbonization, indicative of cellulose degradation in the activated char. Aromatic skeletal C=C vibrations of lignin, typically observed at 1606 $cm^{-1}$and 1514 cm^{-1} (Ghaffar and Fan, 2013), showed an increase in intensity in the activated char. This phenomenon can be interpreted as the preferential accumulation of arene structures from lignin, as well as the generation of new aromatic and carbonized materials resulting from the dehydration of hydrocarbon rings during carbonization.

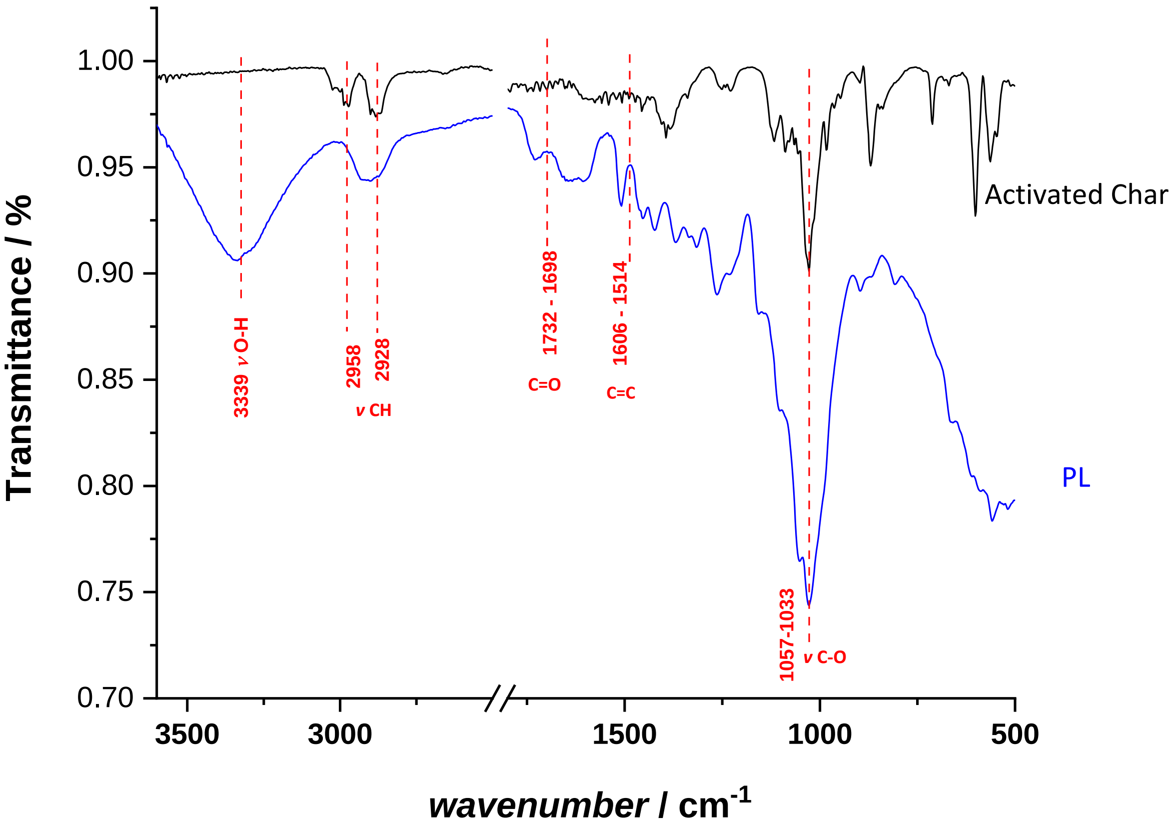

Figure 47: *ATR-IR analysis of activated ST-char*

4.6.5 Scanning Electron Microscopy of ST-activated chars

SEM images of activated ST-char was taking and the result is presented in Figure 48 below. The results shows that activated ST-char are of fine particles and the contain large amount of pores. This results confirm the large amount of pores detected during the mercury porosimetry test.

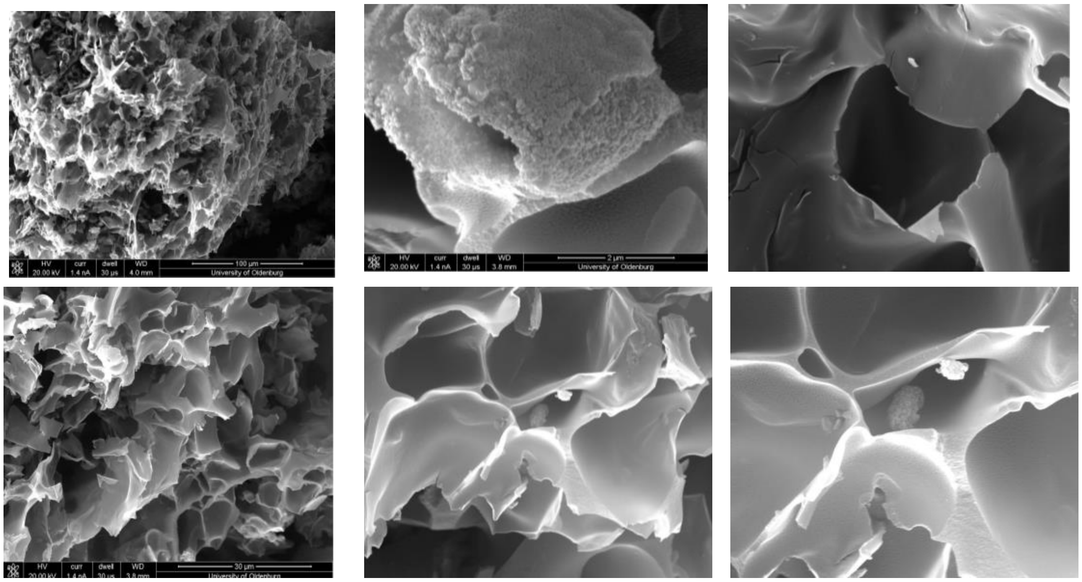

Figure 48: *SEM images of activated ST-char (Sawdust)*

4.7 Analysis of PYC activated char

4.7.1 Nitrogen Sorption Analysis of PYC

The pyrolytic pretreatment was formulated with the aim of producing activated carbon akin to that generated through steam (ST) utilization, while concurrently addressing the drawbacks associated with employing steam at high temperatures during carbonization. In this experimental design, the selected feedstock exclusively comprised sawdust. This choice was motivated by the elevated high ash content observed in the constituent of chicken manure when subjected to high temperature treatment. The initial stage of the experiment focused on the pyrolytic pretreatment of sawdust under varying carbonization durations of 0.5 h and 1 h at a temperature of 750 °C. The process was conducted using different inert gases, namely CO_2 and N_2 along with a condition where no gas was employed (NG). The comprehensive results is reported in Figure 49.

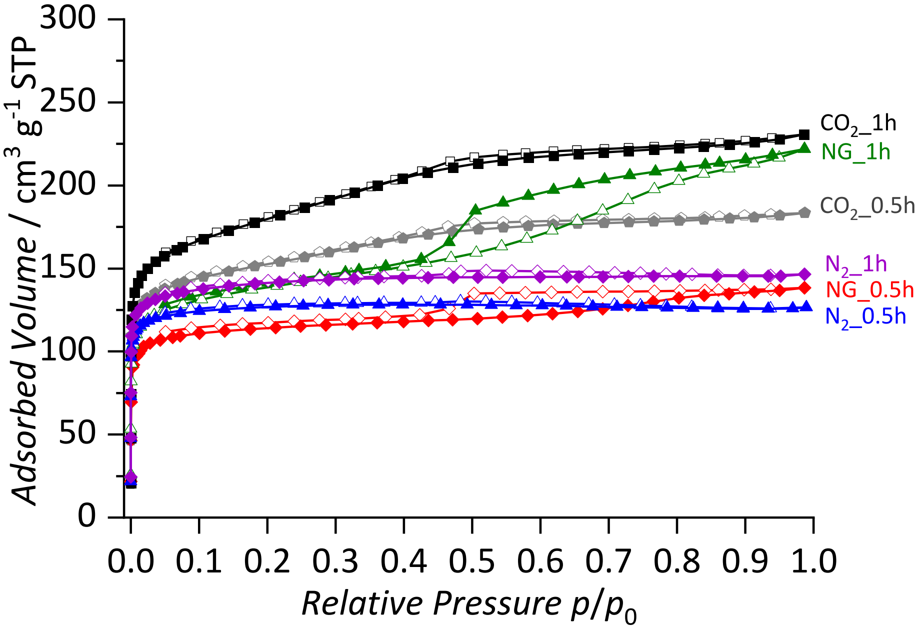

Figure 49: *Pyrolytic pretreatment using CO_2, N_2 and NG*

The outcomes of the experimentation reveal intriguing insights into the pyrolytic pretreatment process. When inert gases are employed during Pyrolytic Carbonization (PYC) treatment, there emerges a distinct possibility of producing PYC-char characterized by substantial mesopore content. Notably, the results also indicate that, irrespective of the use of inert gases (or absence thereof in the case of NG), the potential exists to generate enhanced PYC-char with significant mesopore development. An interesting observation is drawn from the comparison of PYC-char produced using CO_2 for 1 h, which exhibited superior hysteresis containing a mesopores area of 133 m^2g^{-1} and a higher surface area of 663 m^2g^{-1} in comparison to other PYC-char variants produced. Conversely, PYC-chars derived from NG treatment for 1 h displayed a surface area of 525 m^2g^{-1} with an elevated mesopore area of 251 m^2g^{-1} surpassing those observed in all other experimental conditions. These findings explain the impact of both inert gases especially CO_2 and the absence of gas (NG) on the resulting mesoporous characteristics of PYC-char. The distinct performances of CO_2 and NG treatments highlight the potential for tailoring the properties of PYC-char through variations in gas environments and treatment durations, offering valuable insights for optimizing the production of mesoporous activated carbon.

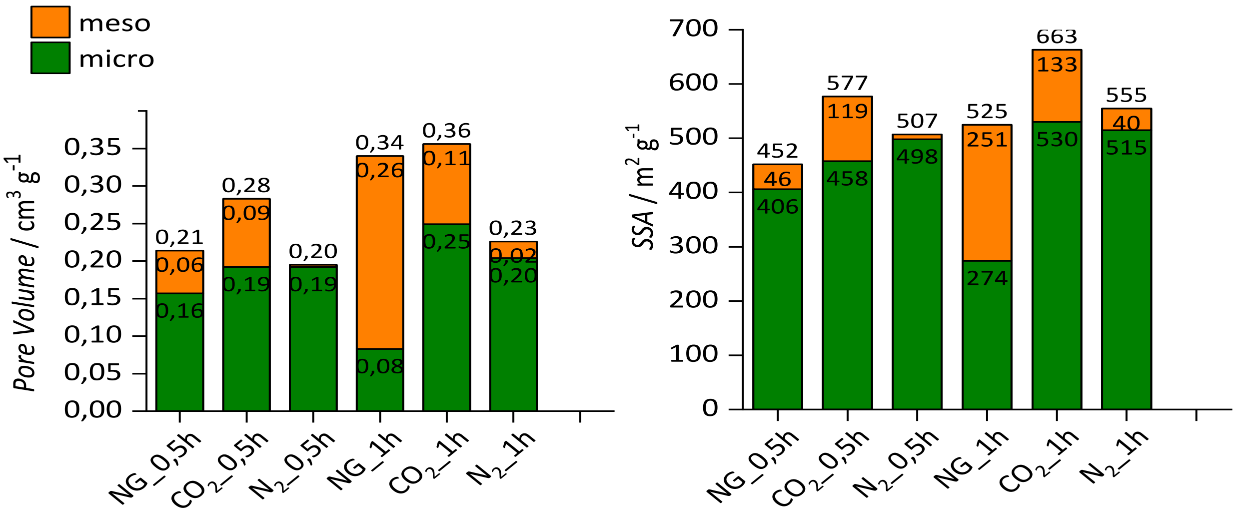

Figure 50: *Surface Area and Pore Volume analysis of PYC*

4.7.2 Yield Analysis of PYC-char

The yield analysis of PYC-chars was conducted to aid in the identification of PYC-char with high yield potential and the result is presented in Figure 51. Notably, PYC-chars produced under a no gas (NG) environment at both 0.5 h and 1 h exhibited impressive yield recoveries, registering at 88 % and 86 %, respectively, surpassing the yield from other methods. Upon closer examination of PYC-char samples with substantial mesopore development, it was observed that NG at 1 h demonstrated a noteworthy mesopore abundance, making it a favourable selection for subsequent activation. Contrastingly, while PYC-char produced with CO_2 displayed elevated surface area and mesopore content, it presented a disadvantage in terms of a markedly lower yield, measured at 15%. This lower yield is attributed to the interaction of CO_2 with the feedstock during pyrolytic pretreatment, resulting in an increased specific surface area (SSA) and subsequently reducing the overall yield. Additionally, alternative methods such as N_2 treatment for 0.5 and 1 h exhibited high yields of 86 % and 85 %, respectively. However, these methods were not considered for selection due to their char properties, which featured an exceptionally low amount of mesopores, measured at 9 and 40 m^2g^{-1}, respectively. The comprehensive assessment of both yield and mesopore development analysis in PYC-char provides valuable insights for the strategic selection of the optimal PYC-char samples for subsequent activation processes, balancing yield considerations with desirable porosity characteristics.

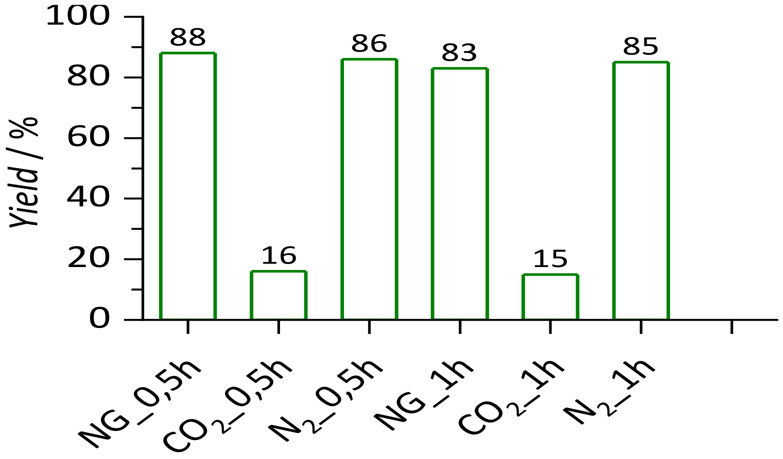

Figure 51: *Yield analysis of PYC*

4.7.3 Nitrogen Sorption Analysis of activated PYC-char

The PYC-char produced using NG at 1 h (NG_1h) emerged as the selected candidate for further analysis, given its commendable yield of 86% and a noteworthy specific mesopores surface area of 251 m^2g^{-1}. This promising PYC-char underwent subsequent steam activation at a temperature of 750 °C for 1 h (Act_NG_1h), and the outcomes are presented in Figure 52. The results demonstrated a compelling transformation post-activation, wherein the porosity of the PYC-char (NG_1h) was significantly augmented. The specific surface area (SSA) experienced a notable increase, soaring from 525 m^2g^{-1} to an impressive 883 m^2g^{-1}. Moreover, the mesopore content exhibited a threefold expansion, escalating from 274 m^2g^{-1} to an impressive 773 m^2g^{-1}. This substantial enhancement in mesopore surface area was accompanied by a parallel increase in pore volumes, surging from 0.34 cm^3g^{-1} to a substantial 0.92 cm^3g^{-1}. These results underscore the efficacy of steam activation in further refining the porosity of the selected PYC-char (NG_1h), resulting in a substantial augmentation of both specific surface area and mesopores development. The tripling of mesopore surface area and pore volumes reflects the successful optimization achieved through steam activation, showcasing the potential for tailoring the characteristics of activated carbon for specific applications.

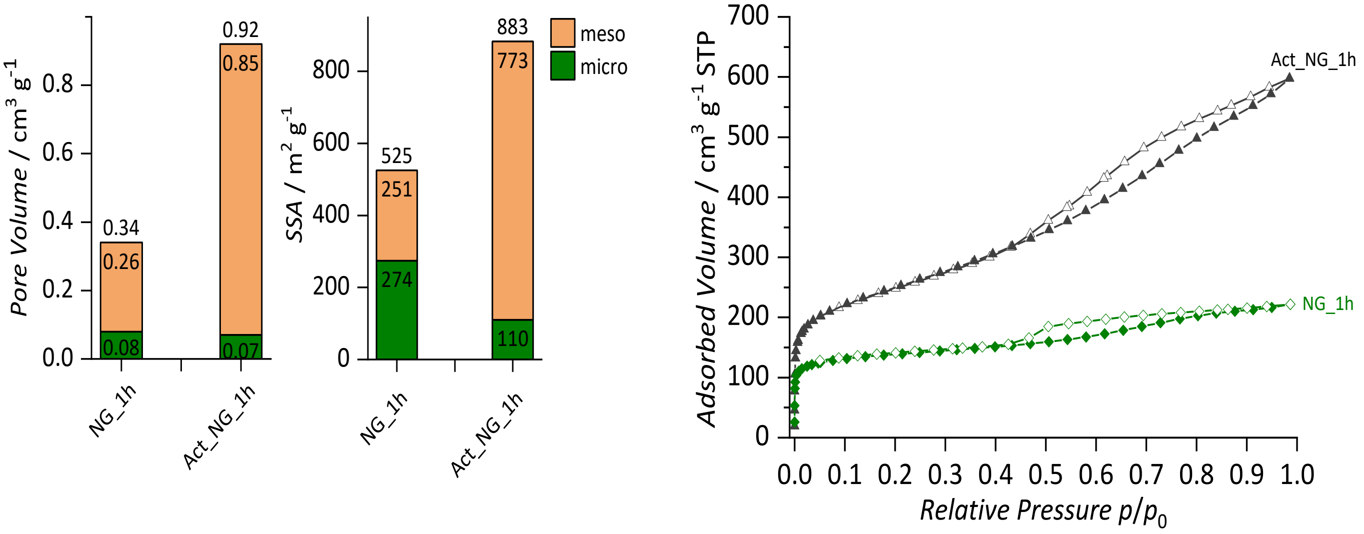

Figure 52: *Activated PYC analysis and Pore development*

4.7.4 Yield Analysis of activated PYC-char

The yield analysis of the selected activated PYC-char was meticulously calculated and juxtaposed with the yield prior to activation. The resultant data, as depicted in Figure 53, revealed a marginal 1 % loss during the activation process. This observation suggests that during Pyrolytic Carbonization (PYC), there was an effective stabilization of the PYC-char, mitigating substantial losses during the subsequent activation stage. The overall yield, encompassing both PYC and activation stages, stood at 85 %, indicating a 15 % loss from the initial starting material to the final production of activated carbon. This comprehensive yield analysis underscores the efficiency of the overall process, where careful management of char stability during PYC contributes to minimizing losses in the subsequent activation step.

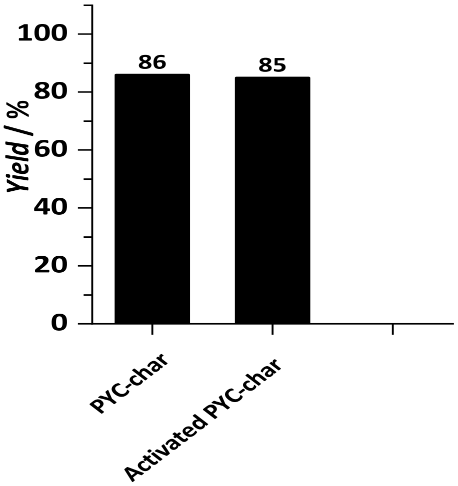

Figure 53: *Yield analysis of PYC-char and activated PYC-char*

4.7.5 Mercury Intrusion porosimetry (Hg) analysis of activated PYC-char

Due to the enormous mesopores present in activated PYC-char, further analysis such Hg intrusion analysis was performed to determine further pore-structure of the activated char. Using the mercury porosimetry, it was possible to detect high macropore volumes for the formed micro-meso-macro-porous activated PYC-char (Figure 54). The result showed activated PYC-char contains macropores volume of about 6.50 cm^3g^{-1} with the initial mesopores volume of 0.85 cm^3g^{-1} and micropores volume of 0.07 cm^3g^{-1} as shown in Figure 10, resulting in a total pore volume of 7.42 cm^3g^{-1}.

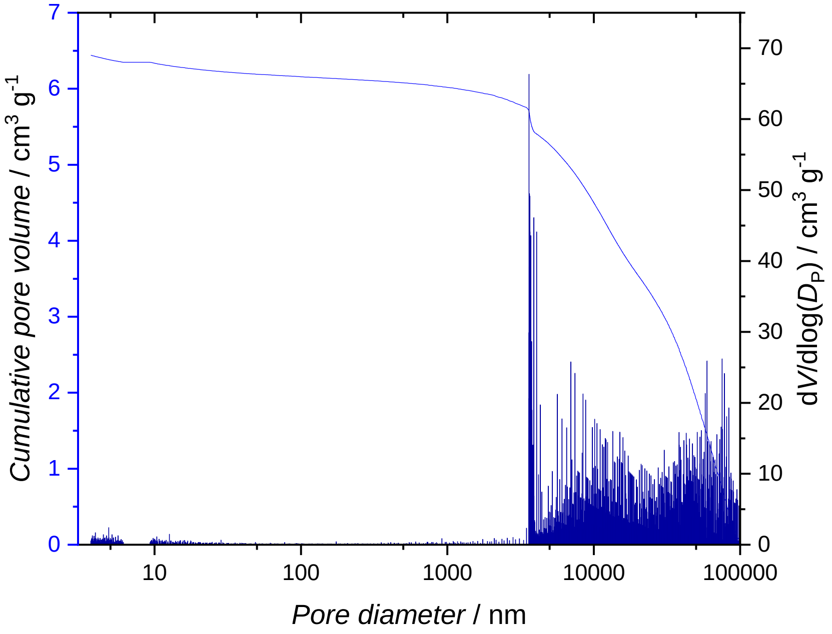

***Figure 54**: Mercury porosimetry analysis of activated PYC-char (Sawdust)*

4.7.6 Scanning Electron Microscopy of activated PYC- chars

SEM images generated for activated PYC-char show similar imaging to the activated ST-char presented, offered a detailed examination of their respective pore structures, as illustrated in Figure 48. Further SEM images of the activated char is presented in Figure 55. Further insights into the particle size distribution were gleaned through additional analysis, as portrayed in Figure 56. Employing the Gauss model, a meticulous evaluation of the particle size distribution was conducted, with the outcomes compiled in Table 11.

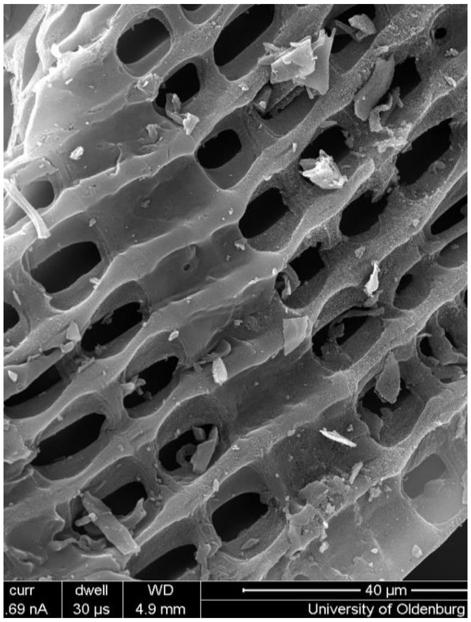

Figure 55: *SEM images of activated PYC-char (Sawdust)*

The results elucidate that the activated PYC-char and ST-char exhibits an average pore size of 9.41 ± 0.75 µm, with a distinct left-skewed distribution. The polydispersity index, approximately 0.16, provides additional context, indicating that the particle size distribution of 9.41 µm is not uniformly spread. This nuanced analysis sheds light on the intricacies of the activated PYC-char's particle size characteristics, offering valuable information for a comprehensive understanding of its pore structure and distribution.

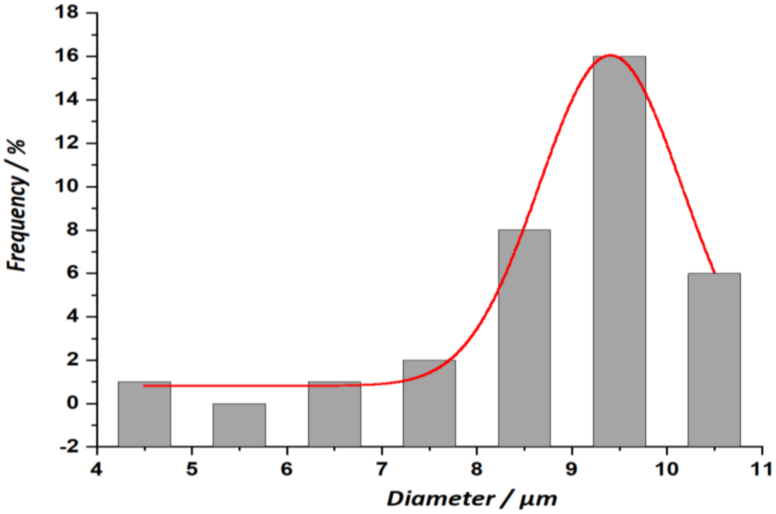

Figure 56: *Pore characterization of activated PYC-char*

Table 11: *Polydispersity derivation Model for activated PYC-char*

Model	Gauss
Equation	$y=y_0 + (A/(w*sqrt(pi/2)))*exp(-2*((x-xc)/w)^2)$
Plot	Counts
y_0	0.81228 ± 0.32362
xc (average pore size)	9.40643 ± 0,03816
w (deviation)	1.4991 ± 0.07442
Standard deviation	$\frac{1.4991}{2} = 0.74955$
Polydispersity	$\frac{0.74955}{9.40643} * 100 = 15.934$

4.8 Comparison of activated char produced

To enhance the comprehension of activated char produced through various carbonization methods, a comparative analysis was conducted by selecting representative activated chars/carbon samples from each of the aforementioned methods detailed in this study. The selection criteria were centered on identifying chars with superior pore structures within each method, thereby facilitating meaningful comparisons across different methods. By focusing on activated chars that exhibited optimal pore structures within their respective methods, this comparative approach aimed to elucidate the variations and similarities in the performance of different thermal carbonization methods. The chosen activated chars were carefully selected to provide insights into the efficacy of each method in terms of pore development and overall structural characteristics. This methodological selection process lays the foundation for a comprehensive understanding of the nuanced outcomes achieved through diverse activation techniques.

4.8.1 Activated char comparison of HTC and VTC

A comparative analysis between activated carbon produced via hydrothermal carbonization (HTC) and vapourthermal carbonization (VTC) was undertaken to discern the impact of water versus vapour in the treatment of poultry litters and the ensuing carbon material production after activation. Despite both methods involving the conversion and treatment of biowaste especially PL, HTC demonstrated a dual capability in producing both 5-HMF and activated carbon, distinguishing it from VTC. HTC showcased its ability to yield ample amounts of 5-HMF through water interactions with PL, contrasting with VTC's reliance on vapour influence. However, this advantage of HTC came at the cost of generating a substantial volume of heavily polluted water (TOC), surpassing that of VTC. While both methods resulted in the production of activated carbon (activated HTC-char and VTC-char), chars produced from VTC exhibited a clearer hysteresis when compared to HTC which indicates a high amount of mesopores. This clarity in hysteresis in VTC-treated chars was attributed to the influence of vapour, which played a role in structuring the arrangement and creating more pronounced pores in the char formation. This results was confirmed by the SEM images showing better and bigger pores after activation in activated chars of VTC as compared to HTC (Figure 57).

Further exploration focused on selected activated carbon produced from S67M33 through VTC, revealing an increasing hysteresis and high specific surface area at elevated pressures. This trend stood in contrast to HTC treatment of similar biowaste (S67M33), indicating distinct structural and adsorption characteristics between the two methods. These comparative findings contribute to a more nuanced understanding of the effects of water and vapour in biowaste treatment especially poultry litters (PL) and the consequent production of activated carbon.

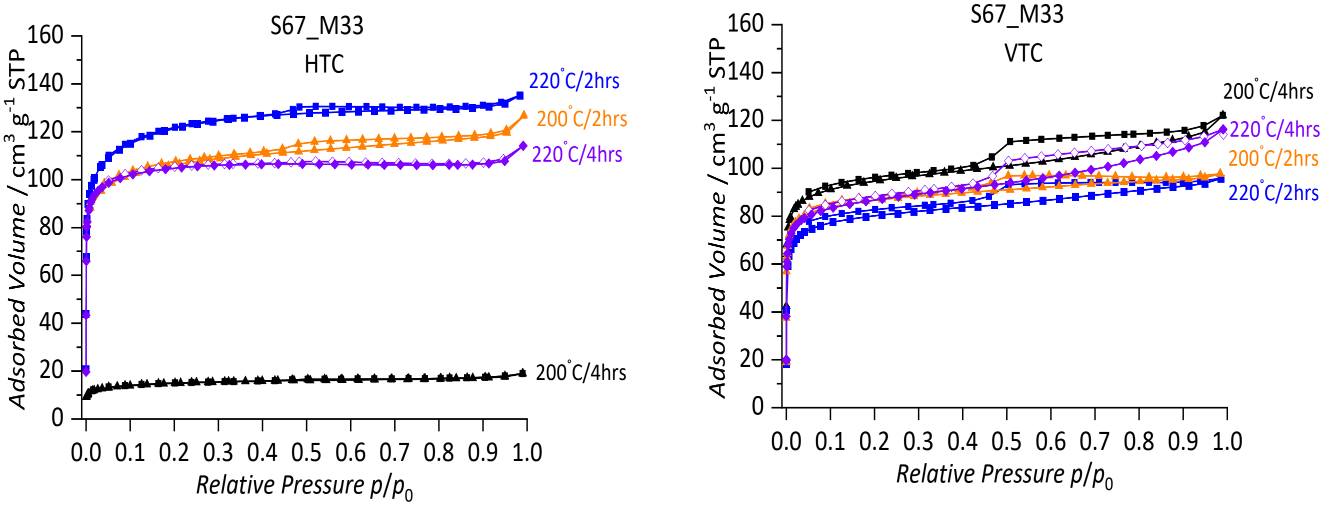

Figure 57 : *HTC and VTC activated char comparison prepared from S67M33*

Consistent trends were also evident in the activated carbon of S50M50 treated with vapourthermal carbonization (VTC). A distinctive and broad hysteresis pattern was observed in the activated carbon produced via VTC in contrast to the usual Hydrothermal Carbonization (HTC). While acknowledging the influence of both methods with their distinct properties, activated chars derived from VTC consistently exhibited higher mesopores, irrespective of the poultry litter constituents. Notably, as process conditions, such as carbonization time, increased from 2 to 4 h during VTC treatment, larger hysteresis patterns leading to higher mesopores were obtained (Figure 58). This stands in contrast to the HTC method, which relies on shorter times for the production of activated chars with relatively limited pore structure (Figure 58).

The clearer hysteresis patterns related to mesopores were notably present in S67M33 and S50M50 during carbonization conditions, further highlighting the distinction between VTC and HTC. These findings explains the impact of process conditions and treatment methods on the resulting pore structures in activated carbon, providing valuable insights for tailoring the production process to achieve desired characteristics.

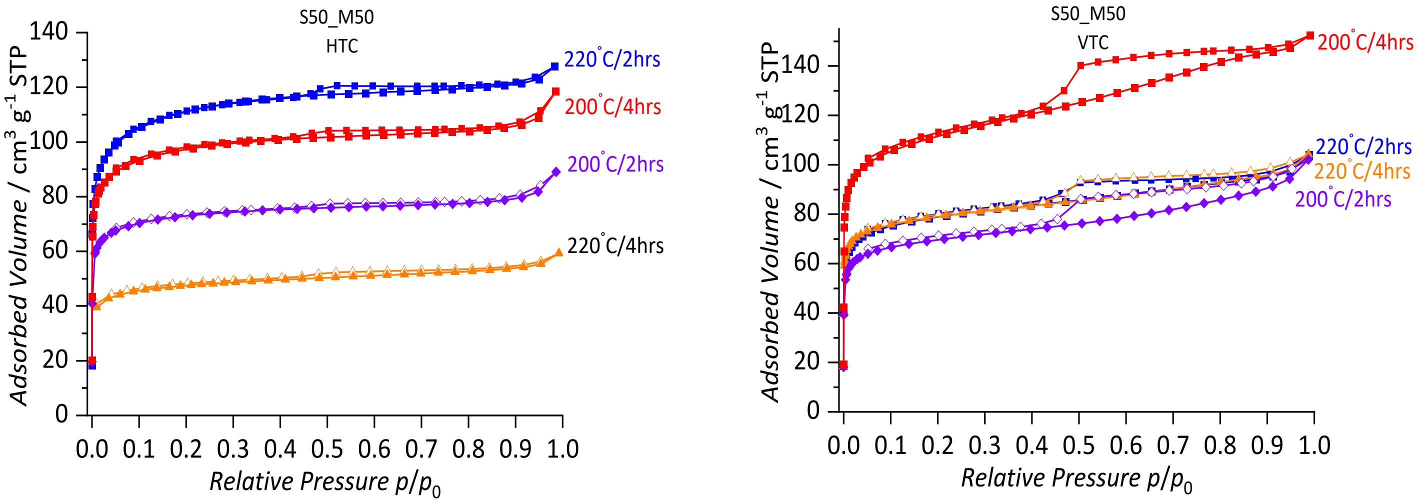

Figure 58: *HTC and VTC activated char comparison prepared from S50M50*

While the impact of prolonged carbonization time was found to be influential in creating more pores in the vapourthermal carbonization (VTC) (Figure 57 and 58). Further exploration delved into varying reaction times during VTC, extending the experimentation period up to 6 hours. The outcomes, as illustrated in Figure 59, unequivocally demonstrated that an extended operating time results in the production of activated carbon characterized by enhanced porosity. This finding explains the significance of the carbonization time in the VTC process, revealing a positive correlation between the duration of the reaction and the quality of porosity in the resulting activated carbon. The systematic analysis of reaction times provides valuable insights for optimizing VTC conditions to achieve superior porosity and, consequently, tailor the properties of activated carbon for specific applications.

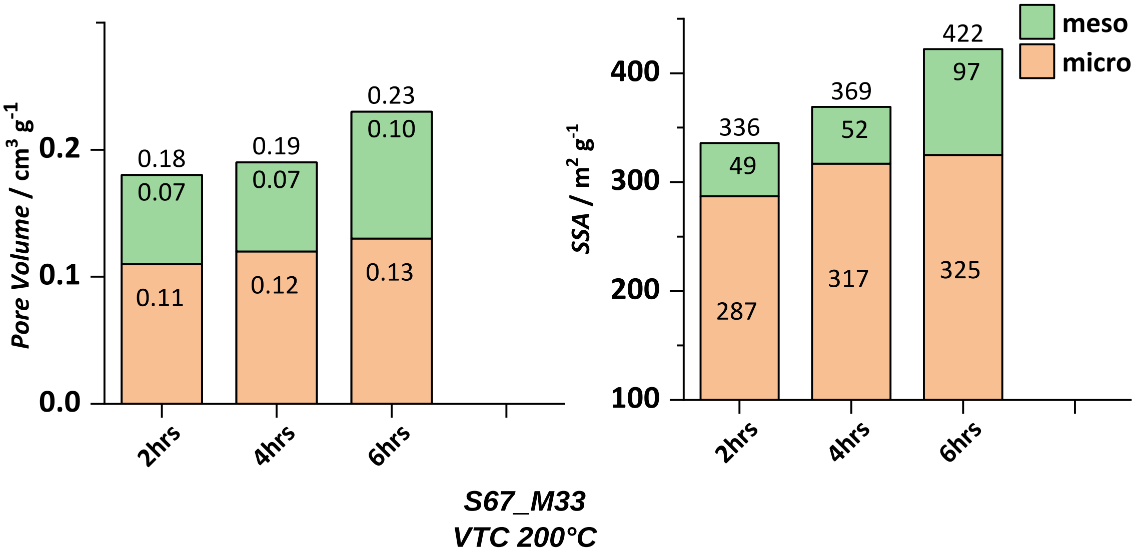

Figure 59: *Influence of prolong VTC carbonization at an increasing time*

4.8.2 Activated char comparison of HTC and ST

Activated carbon production was explored through the conventional hydrothermal carbonization (HTC) method at carbonization conditions of 200 and 220 °C for 2 and 4 hours, resulting in highly porous carbon after subsequent activation at 650 °C. To gain insights into different approaches, similar activated carbon was produced through direct steam (ST) activation of poultry litter (PL) without prior pretreatment at a temperature of 750 °C. Activated carbon/char collected from ST exhibited high porosity, surface area, and volume, regardless of the carbonization conditions. Comparison with activated carbon produced via ST provided a comprehensive understanding of the methodological approaches, as depicted in Figure 60. Notably, attempts to activate hydrochars from HTC at 750°C faced challenges, with most chars transitioning into ash, unlike the more successful ST method.

Results from HTC, after subsequent steam activation, yielded activated chars with microporosity, whereas chicken manure contributed to mesoporosity. This results can be seen in PL with constituent of chicken manure. It was observed that as the amount of chicken manure increases in the PL, so does the amount of mesopores. An opposing trend was observed when activated chars were produced using from PL using direct steam activation (ST) method. Activated chars from direct steam activation exhibited higher pore development, specific surface area (SSA), and pore volume (PV) than activated chars produced from HTC. However, this trend did not hold for scenarios involving a high proportion of chicken manure. In ST, a high amount of sawdust present in the PL were resulting into activated chars with high amount of mesopores.

It was noted that chicken manure aided in the formation of mesoporous carbon in HTC, while poultry litters containing a high amount of sawdust resulted in micropores. Conversely, in activated carbon produced via ST, a large amount of sawdust in poultry litters resulted in mesopores.

Comparative analysis of both methods and the resulting activated chars demonstrated the ability to produce activated carbon with a specific surface area of 824 m^2g^{-1} through ST, surpassing the 660 m^2g^{-1} obtained from sawdust in HTC while for chicken manure, a specific surface area of 488 m^2g^{-1} where produced during HTC surpassing the 216 m^2g^{-1} of ST. These findings highlight the versatility of different carbonization methods and the influence of feedstock composition on the properties of activated carbon or char.

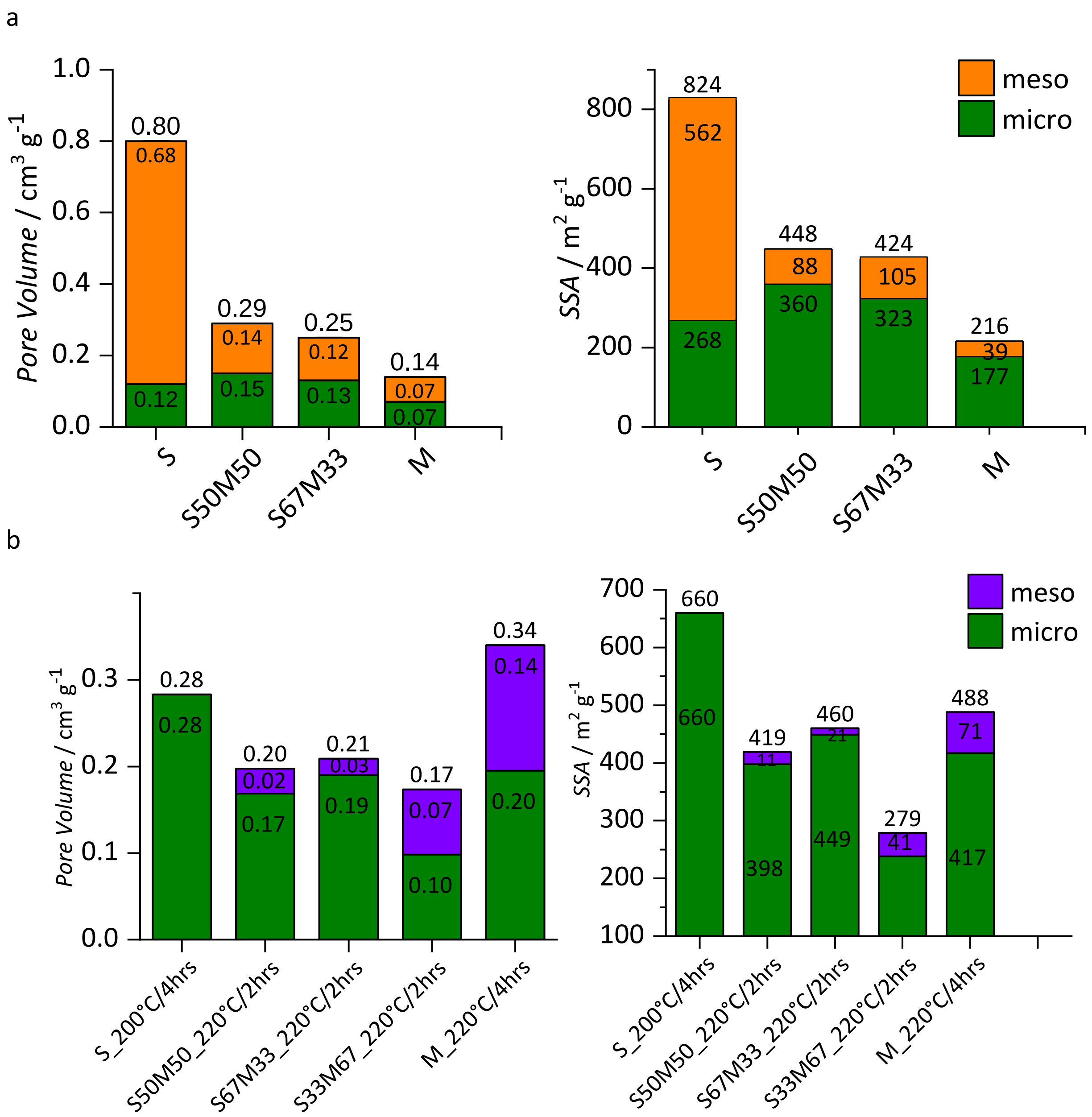

Figure 60: *Activated char comparison of ST (a) and HTC(b)*

4.8.3 Activated char comparison of ST and PYC

Employing similar methodological approaches in both Pyrolytic Carbonization (PYC) and Steam Activation (ST), the primary objective of the PYC method is to generate activated char with a pore structure resembling that of activated char produced via ST. This approach aims to address the low yield associated with ST. The comparison of activated char produced from both methods is presented in Figure 61.

Activated char with similar characteristics was successfully produced using both PYC and ST methods. Comparable hysteresis patterns were observed at increasing pressure levels (Figure 35). PYC demonstrated the ability to generate activated char akin to ST, with a marginal increase in specific surface area from 821 m²g⁻¹ to 883 m²g⁻¹ and pore volumes from 0.83 cm³g⁻¹ to 0.92 cm³g⁻¹. The pore distribution in nitrogen sorption curves along relative pressure showcased similar structures between the two methods. Yield analysis revealed that PYC enabled the production of a similar activated char with a high yield compared to ST. While ST was associated with a very low yield of 18 %, PYC increased the yield to approximately 85 %, resulting in about a 15 % loss in the starting material during PYC, in contrast to the 82 % loss during ST. These findings underscore the efficacy of PYC in achieving comparable activated char properties while addressing the yield limitations associated with ST.

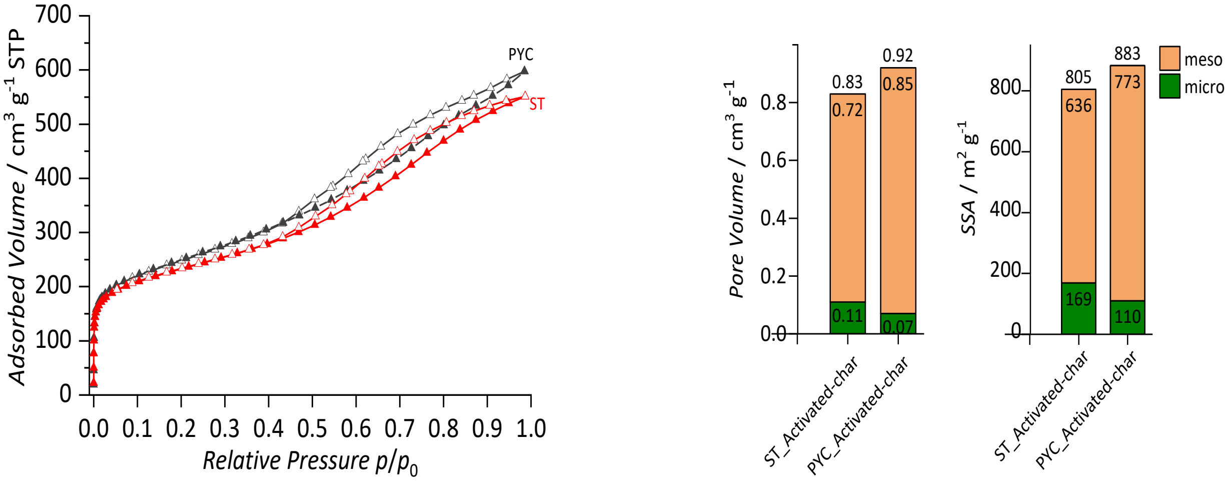

Figure 61: *Activated char comparison of ST and PYC*

4.9 Application of activated char

4.9.1 Carbon electrode material in Na ion batteries

Figure 62 illustrates the capacitance results of carbon electrodes developed from activated chars derived from Hydrothermal Carbonization (HTC) and Steam from high temperature (ST), in comparison with an industrially purchased carbon black electrode (Super_P). The findings indicate that the carbon electrode from HTC exhibits lower capacitance than the Super_P electrode. Specifically, the HTC carbon electrode, particularly from sawdust with a specific surface area (SSA) of 660 m^2g^{-1} and approximately 99.8 % micropores, demonstrates a reduced capacitance in comparison to Super_P with an SSA of 54 m^2g^{-1} and 91 % mesopores. This discrepancy suggests that micropores with ultrafine pore size pose challenges for the utilization of electrolyte ions, regardless of their SSA. In this case, the typical relationship between SSA and capacitance is not applicable due to the predominance of micropores in activated carbon prepared from HTC and the limited presence of mesopores.

However, the electrode material from ST, with an SSA of 824 m^2g^{-1} and containing about 68 % mesopores, exhibits a larger capacitance than Super_P with 54 m^2g^{-1} SSA and 91 % mesopores (as shown in Fig. 9). This result establishes a clear relationship between SSA and capacitance. The observed relationship between ST and Super_P further supports the assertion that there is a correlation between specific capacitance and the SSA of the carbon electrode containing a high amount of mesopores. However, this correlation does not apply to HTC, primarily due to the morphology of activated HTC chars, which predominantly consist of micropores compared to other methods such as ST which consist more pore development above micropores. Similar findings were reported by Zhou et al. (2007), where the influence of SSA and mesoporosity of activated carbon was observed to affect the capacity in sodium-ion batteries.

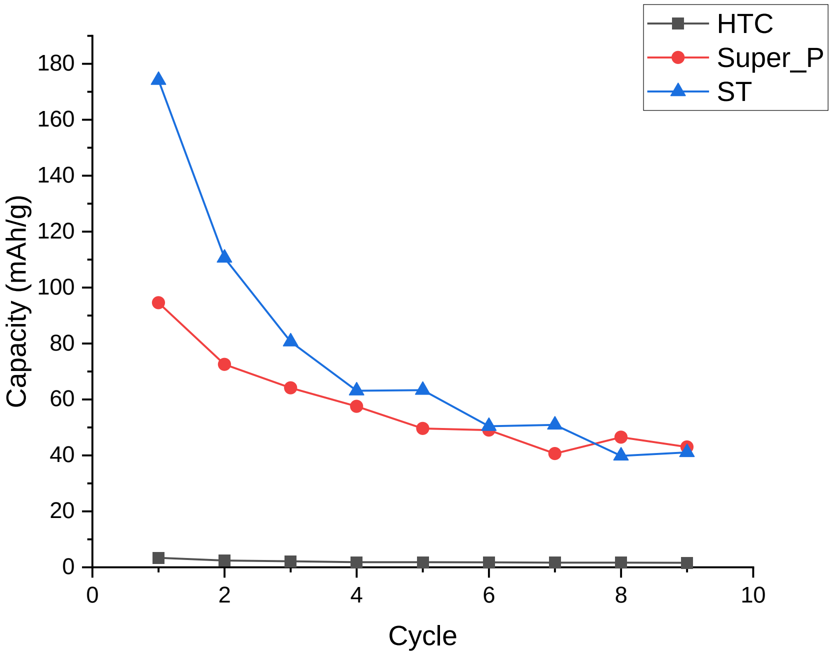

Figure 62: *Capacitance of electrode material*

4.9.2 Methylene blue dye adsorption

Selected activated char was employed for the absorption of methylene blue dye, aiming to explore potential applications of activated chars in water purification. In this experiment, 100 g of methylene blue was dissolved in 50 ml of water using 40 mg of activated char, with the total absorption measured over 300 minutes.

Figure 63: Methylene Blue Dye Absorption

The results revealed that methylene blue was completely absorbed by activated chars derived from Steam (ST) and Pyrolytic Carbonization (PYC) in approximately 60 minutes. This indicates a notable efficiency in water purification tendencies for activated chars produced from steam or vapour when compared to those derived from Hydrothermal Carbonization (HTC) due to their pore structure. In contrast, activated chars from HTC displayed insignificant dye absorption even after 300 minutes. The findings suggest that activated chars prepared with a high amount of meso-macro pores, as seen in ST, PYC and VTC, exhibit promising potential for water treatment applications. This highlights the diverse capabilities of activated chars from different carbonization methods and their suitability for specific environmental remediation purposes.

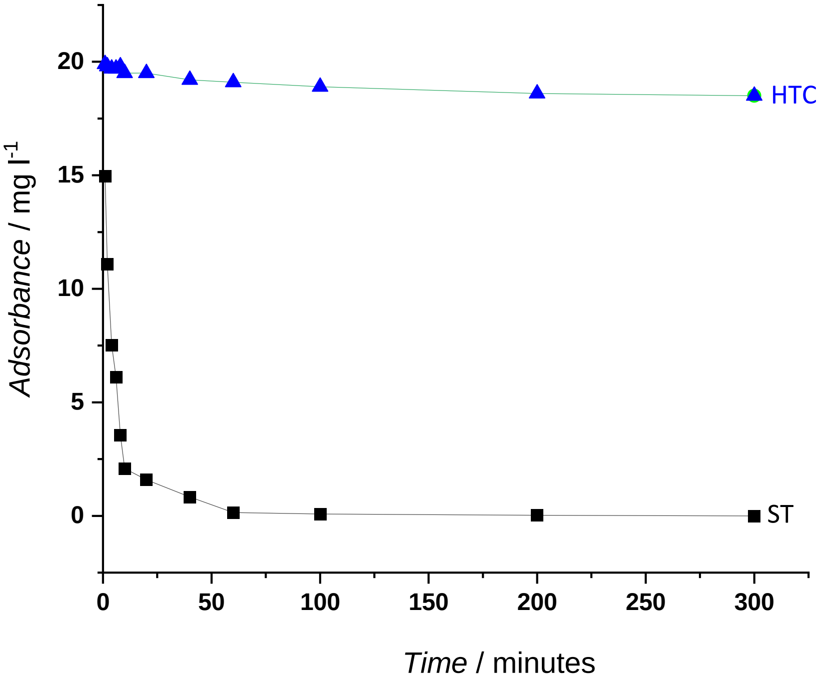

Figure 64: *Dye absorbance per minutes*

4.10 References

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T. Wang et al. Renewable and Sustainable Energy Reviews 90 (2018) 223–247.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In the pursuit of a waste-free technology, this study has successfully pioneered advancements in biowaste conversion through various carbonization methodologies, including hydrothermal carbonization (HTC), two-step HTC, vapourthermal carbonization (VTC), steam treatment (ST), and pyrolytic carbonization (PYC). The focus on diverse feedstocks, particularly poultry litters (PL) comprising sawdust and chicken manure, has unveiled promising avenues for value-added chemical production and carbon material synthesis.

The investigation into HTC demonstrated its efficacy in yielding 5-Hydroxymethylfurfural (5-HMF), a valuable chemical, with the proportion of sawdust in the poultry litters exerting a significant influence. However, the optimization of 5-HMF production to an impressive 16.3 g/l was achieved through the innovative two-step HTC method. This not only showcased the potential of this approach in enhancing chemical yields but also contributed to the reduction of total organic carbon (TOC) in the process water, addressing a critical environmental concern associated with HTC.

Activated chars derived from HTC at 650 °C were subjected to thorough characterization, revealing a noteworthy outcome. The presence of a higher proportion of chicken manure in the poultry litters led to the production of mesoporous carbon, emphasizing the critical role of feedstock composition in tailoring pore structures. Interestingly, this trend diverged in the case of steam treatment (ST), where the emphasis shifted towards sawdust for optimal porosity. Vapourthermal carbonization (VTC), employing vapour, exhibited a distinct approach, yielding highly porous carbon without the burden of excessive process water, setting it apart from HTC and two-step HTC.

Furthermore, an improvised pyrolytic carbonization (PYC) treatment addressed the low yield associated with ST, showcasing the potential for methodological enhancements to overcome inherent limitations. The comparison of these diverse methods highlighted the versatility of VTC, offering micro-meso-macro pore structures and circumventing challenges present in other approaches.

In the grand panorama of waste-to-value technologies, the conclusions drawn from this research underscore the significance of methodological intricacies and feedstock nuances. VTC emerges as a promising contender, and the two-step HTC stands out as an effective tool for optimizing chemical yields while simultaneously mitigating environmental concerns. As we venture towards sustainable solutions, the amalgamation of diverse technologies and strategic feedstock management paves the way for a transformative shift in biowaste utilization. This study does not only contributes to the scientific understanding of carbonization processes but also advocates for a paradigm shift towards eco-friendly technologies with a focus on minimizing environmental impact and maximizing resource efficiency.

5.2 Recommendations

The following recommendations aim to guide future research, industrial practices, and policy decisions toward more sustainable and efficient waste-to-value technologies, fostering a transition to a circular and eco-conscious economy.

1. Embrace two-Step HTC for optimal chemical yields: The two-step HTC method demonstrated remarkable potential in optimizing 5-Hydroxymethylfurfural (5-HMF) production while mitigating environmental concerns associated with Hydrothermal Carbonization (HTC). Future studies and industrial applications should explore and adopt this innovative approach for enhanced chemical yields and reduced environmental impact.
2. Promote vapourthermal carbonization (VTC) for versatile porosity: VTC, with its ability to produce highly mesoporous carbon without excessive heavily polluted process water, stands out as a transformative methodology. Further research and development efforts should focus on exploring the diverse applications of the meso-, macro- porous carbon synthesized through VTC, particularly in water treatment and energy storage applications.
3. Tailor feedstock composition for desired pore structures: The findings underscore the influence of feedstock composition on pore structures in the produced carbon materials. Researchers and practitioners should consider tailoring the composition of poultry litters to achieve specific pore structures, depending on the intended application.

4. Investigate further improvements in pyrolytic carbonization (PYC): The improvised PYC treatment showed promise in addressing the low yield associated with steam treatment (ST). Further investigations and refinements in the PYC process could lead to a more efficient method for producing activated carbon with improved yield and desirable pore properties
5. Explore application-specific utilization of HTC-derived carbon: While HTC-derived carbon exhibited limitations in mesoporous structure, certain applications resonated with its unique properties. Researchers should explore niche applications where HTC-derived carbon can find utility, recognizing its strengths and limitations.
6. Optimize carbon production with steam activation: Exploring the innovative methods to enhance meso-, macro porous carbon production using steam activation. While the current process exhibits low yield, the high meso and macro porosity make it promising for applications such as water treatment. Investigating ways to diversify feedstocks, particularly by developing techniques that allow increased utilization of other plant biomass and transition toward incorporating higher amounts of animal manure. Additionally, prioritizing of the research efforts to streamline and expedite the production process, positioning steam activation as a time-efficient method in the realm of carbonization technologies.
7. Integrate diverse carbonization technologies for comprehensive solutions: The amalgamation of diverse carbonization methodologies, each with its unique strengths, offers a comprehensive approach to waste valorization. Future research should focus on integrating these technologies strategically to harness the synergies and address specific challenges associated with each method.
8. Promote eco-friendly practices in waste management: This study advocates for a paradigm shift toward sustainable, eco-friendly waste-to-value practices. Industries and policymakers should consider adopting technologies like VTC and Two-step HTC to minimize environmental impact and maximize resource efficiency.
9. Encourage interdisciplinary collaboration: Given the multifaceted nature of waste-to-value technologies, interdisciplinary collaboration is crucial. Researchers from diverse

fields, including chemistry, environmental science, and engineering, should collaborate to bring about holistic solutions to the challenges associated with biowaste conversion.

CHAPTER SIX

6.0 PUBLICATIONS AND CONFERENCE

6.1 Publications

1. Henrike Schmies, Nina Bengen, Julia Müller-Hülstede, **Olayinka Ahmed Ibitowa**, Peter Wagner and Michael Wark (2023). How Effective Is Graphitization of Biomasses for the Carbon Stability of Pt/C ORR Catalysts? https://www.researchgate.net/publication/368190000_How_Effective_Is_Graphitization_of_Biomasses_for_the_Carbon_Stability_of_PtC_ORR_Catalysts
2. Rafail Isemin, Natalia Muratova, Sergey Kuzmin, Dmitry Klimov, Vadim Kokh-Tatarenko, Alexander Mikhalev, Oleg Milovanov, Antoine Dalibard, **Olayinka Ahmed Ibitowa**, Manuel Nowotny, Mathieu Brulé, Fouzi Tabet and Bernd Rogge (2021). Characteristics of Hydrochar and Liquid Products Obtained by Hydrothermal Carbonization and Wet Torrefaction of Poultry Litter in Mixture with Wood Sawdust. https://www.researchgate.net/publication/356412083_Characteristics_of_Hydrochar_and_Liquid_Products_Obtained_by_Hydrothermal_Carbonization_and_Wet_Torrefaction_of_Poultry_Litter_in_Mixture_with_Wood_Sawdust_Characteristics_of_Hydrochar_and_Liquid_Prod
3. **Ibitowa, Olayinka Ahmed** and Wark, Michael (2022). Dataset on nitrogen adsorption and desorption isotherms of activated carbon prepared from poultry litters, Mendeley Data, V1, doi: 10.17632/hjnhzkj67k.1. https://data.mendeley.com/datasets/hjnhzkj67k/1

6.2 Conference

1. **Olayinka Ahmed Ibitowa**, Bjorn Müller and Micheal Wark (2022). Highly porous carbon-based electrodes with enhanced properties for application in sodium-ion batteries. 7th Forum on Hydrothermal Processes. https://www.dbfz.de/en/7th-expert-forum-on-hydrothermal-processes/program-26-november-2020

APPENDIX

Dataset regarding this reasearch are published and can be found on:

Ibitowa, Olayinka Ahmed and Wark, Michael (2022). Dataset on nitrogen adsorption and desorption isotherms of activated carbon prepared from poultry litters, Mendeley Data, V1, doi: 10.17632/hjnhzkj67k.1.

https://data.mendeley.com/datasets/hjnhzkj67k/1